

Program and Abstract Volume

The New Martian Chemistry Workshop

*July 27–28, 2009
Medford, Massachusetts*

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Preface

This volume contains abstracts that have been accepted for presentation at the New Martian Chemistry Workshop, July 27–28, 2009, Medford, Massachusetts.

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Monday, July 27, 2009
INTRODUCTION
8:30 a.m. Alumni Lounge

- 8:30 a.m. Welcome, Workshop Logistics, and Agenda
- 8:35 a.m. Hecht M. H. *
Introduction to New Martian Chemistry Workshop: "Follow the Chemistry" [#8030]

RESULTS FROM THE PHOENIX MISSION

- 8:40 a.m. Hecht M. H. * MECA Team **[INVITED]**
Overview of the Phoenix Mission, TECP, and Microscopy
- 9:00 a.m. Sutter B. * Ming D. W. Boynton W. V. Niles P. B. Hoffman J. Lauer H. V. Golden D. C.
Summary of Results from the Mars Phoenix Lander's Thermal Evolved Gas Analyzer [#8004]
- 9:20 a.m. Kounaves S. P. * Hecht M. H. Anderson R. Gospodinova K. Hredzak P.
Kapit J. Maisano J. McElhoney K. Moore Q. O'Neil G. Shusterman J.
Stroble S. Wage J
*Aqueous Chemistry of the Martian Soil: Recent Results from the Phoenix Mars Lander
Wet Chemistry Laboratory (WCL) [#8020]*
- 9:40 a.m. Hurowitz J. A. *
What Would MER Soil do in the Phoenix WCL? [#8006]

Monday, July 27, 2009
RESULTS FROM ORBIT
10:00 a.m. Alumni Lounge

- 10:00 a.m. Bishop J. L. * McKeown N. K. Mustard J. F. Buczkowski D. L. Clark R. N.
Des Marais D. J. Ehlmann B. L. Marzo G. Milliken R. E. Murchie S. L. Noe Dobrea E. Z.
Parente M. Roush T. L. Swayze G. A. Wray J. J. CRISM Team
Distribution and Variability of Phyllosilicates on Mars Observed by MRO/CRISM and What They Can Tell us About Early Martian Chemistry [#8003]
- 10:15 a.m. Bandfield J. L. * Rogers A. D. Edwards C. S.
The Role of Aqueous Alteration in the Formation of Martian Soils [#8007]
- 10:30 a.m. BREAK
- 10:45 a.m. Roach L. H. * Mustard J. F. Murchie S. L. Bishop J. L.
Sulfates in Valles Marineris and Implications for Mars' Aqueous History [#8027]
- 11:00 a.m. Ehlmann B. L. * Mustard J. F. CRISM Team
Regional Carbonate- and Kaolinite-bearing Rock Units and How Precursor Lithologies Control Alteration Products on Mars: An Example from the Nili Fossae Region [#8018]
- 11:15 a.m. Levy J. S. * Head J. W. Marchant D. R.
Geomorphology of High-Latitude, Ice-rich Surfaces on Mars: Constraints on the Age, Thermal State, and Landscape Processes Active in Vicinity of Phoenix and the Martian Latitude-dependent Mantle [#8015]
- 11:30 a.m. Horgan B. * Bell J. F. III
Acid Alteration of Basaltic Sand: Formation of a Major Martian Surface Type [#8023]
- 11:45 a.m. **Moderated Panel Discussion**
- 12:15 p.m. **Catered Lunch and Guest Speaker**

Monday, July 27, 2009
SOIL CHEMISTRY: AQUEOUS PROCESSES ON EARTH AND MARS
1:00 p.m. Alumni Lounge

- 1:00 p.m. Tosca N. J. *
The Chemistry of Martian Water After ~3 Gyr of Planetary Evolution [#8025]
- 1:15 p.m. Des Marais D. J. *
Potential Lifestyles in Ancient Environments Characterized by the Mars Exploration Rovers [#8031]
- 1:30 p.m. Bao H. *
Isotopic Analysis of Salts in Terrestrial Hyper-Arid Deserts: Analogs for Understanding the Origin and Mobility of Salts on Mars [#8028]
- 1:45 p.m. Chadwick O. A. * Amudson R.
Desert Soils and Mars [#8029]
- 2:00 p.m. Niles P. B. * Michalski J.
Closed System Chemistry Inside Massive Ice Deposits at Meridiani Planum [#8013]
- 2:15 p.m. **Moderated Panel Discussion**
- 2:45 p.m. BREAK

Monday, July 27, 2009
PERCHLORATE: VOLATILES AND PHOTOCHEMISTRY
3:00 p.m. Alumni Lounge

- 3:00 p.m. Catling D. C. * Claire M. W. Zahnle K. J. Quinn R. C. Clark B. C.
Hecht M. H. Kounaves S. P.
Perchlorate Origins in the Atacama and on Mars [#8021]
- 3:15 p.m. Chevrier V. F. * Hanley J.
*Thermodynamic Properties of Oxidized Forms of Chloride and Applications to the
Phoenix Surface Chemistry* [#8009]
- 3:30 p.m. Hanley J. * Chevrier V. F.
Hydrous Perchlorates and Their Relation to Humidity at the Phoenix Landing Site [#8008]
- 3:45 p.m. Rivera-Valentin E. G. Chevrier V. F. *
*Time Dependent Model for Water Vapor Diffusion/Adsorption and Heat Transfer at the
Phoenix Landing Site* [#8016]
- 4:00 p.m. **Moderated Panel Discussion**
- 4:30 p.m. **Wrap Up: The Big Questions, Part I**
- 5:00 p.m. Adjourn

Tuesday, July 28, 2009
INTRODUCTION
8:30 a.m. Alumni Lounge

8:30 a.m. Update, Workshop Logistics, and Agenda

ASTROBIOLOGY

- 8:45 a.m. Coleman M. *
Perchlorate on Earth and Mars, Formation Processes, Fate, Implications for Astrobiology and Suggestions for Future Work [#8024]
- 9:00 a.m. Aubrey A. D. * Parker E. T. Grunthaner F. J. Bada J. L.
Implications of the Presence of Surface Perchlorate for In Situ Detection of Organic Compounds During Future Missions [#8005]
- 9:15 a.m. Howe K. L. Gavin P. Kral T. A. Goodhart T. Chevrier V. *
Methanogen Growth in Perchlorate-supplemented Media and Implications for Life in Phoenix-Type Soils [#8014]
- 9:30 a.m. Sun H. J. *
Substrate Stereo Selectivity May be Used to Distinguish Between Chemical and Biological Reactivity on Mars [#8022]
- 9:45 a.m. **Moderated Panel Discussion**
- 10:15 a.m. BREAK

Tuesday, July 28, 2009
FUTURE MISSIONS AND EXPERIMENTS
10:30 a.m. Alumni Lounge

- 10:30 a.m. Blake D. F. * Bish D. L. Chipera S. J. Vaniman D. T. Sarrazin P. CheMin Team
In Situ Analysis of Hydrous and Aqueous Minerals Using the CheMin Mineralogical Instrument on Mars Science Laboratory [#8026]
- 10:45 a.m. Dyar M. D. * Tucker J. M. Clegg S. M. Schaefer M. W. Wiens R. C. Barefield J. E. II.
Probing Martian Surface Chemistry with LIBS: Major and Minor Element Analyses with Laser-induced Breakdown Spectroscopy [#8019]
- 11:00 a.m. Grady M. M. * Tomkinson T. Wolters S. D. Guthery W. Bohman A. F. Sund A. T.
WATSEN — A Mid-IR Spectrometer, Humidity Sensor and Optical Microscope to Identify the Subsurface Water and Mineralogy of Mars [#8012]
- 11:15 a.m. **Moderated Panel Discussion**
- 11:45 a.m. **Wrap Up: The Big Questions, Part II**
- 12:15 p.m. LUNCH

Tuesday, July 28, 2009
WORKING SESSIONS – BREAKOUT AND WRAP UP
1:30 p.m. Alumni Lounge

- 1:30 p.m. Breakout Groups
- 2:30 p.m. BREAK
- 2:45 p.m. Breakout Group Reports: Group Leaders
- 3:15 p.m. Strategy for Future Exploration: Moderator (Hecht)
- 4:15 p.m. Planning for MEPAG and White Paper: Moderator (Kounaves)
- 5:00 p.m. Adjourn

POSTER DISPLAY
Alumni Lounge

*The following presentations will be available as poster displays
(with no formal poster session) at the workshop.*

Berger G. Meunier A.

The Out-Gassing of a Basalt Flow as a Source of Martian Phyllosilicate [#8001]

Hanley J. Chevrier V. F. Davis B. L. Altheide T. S. Francis A.

Reflectance Spectra of Low-Temperature Chloride and Perchlorate Hydrates and Their Relevance to the Martian Surface [#8010]

Richardson C. D. Hinman N. W. Kotler J. M. McJunkin T. R. Scott J. R.

Influence of Geochemistry on Detection of Bio/Organic Signatures [#8017]

Tomkinson T. Needham A. W. Grady M. M. Hagermann A. Wright I. P.

Understanding the Evolution of Martian Carbonates from a Combined Modelling and Synthesis Study [#8011]

IMPLICATIONS OF THE PRESENCE OF SURFACE PERCHLORATE FOR *IN SITU* DETECTION OF ORGANIC COMPOUNDS DURING FUTURE MISSIONS. A. D. Aubrey¹, Eric T. Parker², F. J. Grunthaner¹ and J. L. Bada², ¹NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Andrew.D.Aubrey@jpl.nasa.gov; Frank.J.Grunthaner@jpl.nasa.gov), ²Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA (erictparker@gmail.com; jbada@ucsd.edu).

Introduction: One crucial discovery by the 2009 NASA Phoenix Lander was the detection of perchlorate at ~1% in the surface Martian regolith [1]. High concentrations of perchlorate may oxidize organics on Mars and be problematic during extraction of organics during future *in situ* investigations. High temperature pyrolytic extraction methods will likely result in catalytic degradation of organics [2] especially in the presence of oxidants or transition metals. If simulant studies reveal Martian soil chemistry to be incompatible with the survival of organics during pyrolytic extraction, then *in situ* instruments should utilize techniques that will not catalyze degradation during thermal volatilization (TV).

Atacama Desert soils are known to contain large abundances of perchlorate [3], most likely derived from atmospheric photochemical deposition [4]. Previous GCMS analysis of samples from the hyperarid core of the Atacama Desert reported no organics above ppb-levels and claimed that this hyperarid region represented the dry limit for microbial life [5]. Amino acids at ppb-levels are detectable in the majority of samples from this region using subcritical water extraction (SCWE). It is unknown whether amino acid abundances are impacted by the presence of surface soil oxidants such as perchlorate in the Atacama.

Discussion: Subcritical water extraction (SCWE) of amino acids has been successfully demonstrated on a variety of Atacama Desert soils (Fig 1) with high efficiencies compared to traditional quantification *via* acid hydrolysis. The characteristics of SCWE as a non-destructive and efficient extraction method is the reason it is the primary extraction step for the *Urey* organic detector [6] while it also may be integrated as a subsystem for other *in situ* instruments.

Amino acid distributions and enantiomeric ratios can be used to determine whether their source is extant microbial life or diagenetic products of extinct life. Atacama Desert subsurface samples (>5 cm depth) show much better preservation of microbial biosignatures, and this has been interpreted as enhanced organic preservation *via* shielding from harsh surface conditions (e.g. destruction by UV-radiation, fenton oxidation, free radicals). It is unknown whether degradation of organics by surface oxidants, such as perchlorate, act as leveling reactions in the Atacama Desert. In order to examine whether amino acid abundances and distributions are affected by perchlorate concentrations, $[\text{ClO}_4^-]$ is currently being measured by ion chromatography (IC) within these Atacama Desert

samples. Perchlorate concentrations are expected to be in low-ppm range due to levels observed in previous studies [3] and the extremely arid climate which enhances perchlorate deposition.

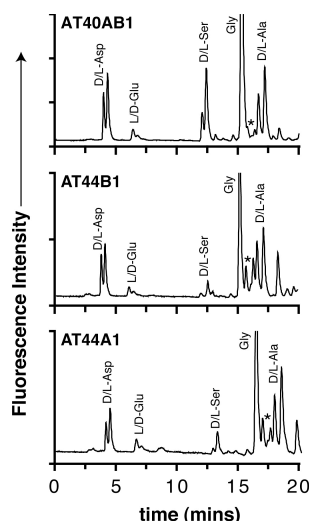


Fig 1. 0-20 minute HPLC chromatograms of subcritical water extracted Atacama Desert surface soil samples. Amino acids and their enantiomers are labeled while the asterisk represents the identification of two amino acid decarboxylation products, β -ala and γ -aba. These peaks are evidence of diagenetic processes in surface samples.

Conclusion: Results indicate that SCWE liberates amino acids from Atacama Desert soils quickly and efficiently despite the presence of perchlorate. Aqueous heating experiments at 100°C show minor differences in the rates of amino acid degradation over timescales of weeks, and therefore perchlorate should minimally effect SCWE at the short exposure times characteristic of these optimized extraction conditions [7]. Pyrolytic methods such as thermal volatilization (GCMS) may activate oxidants present in the Mars regolith and catalyze organic degradation [2] resulting in a false negative for organic compound detection. It may be necessary to adopt non-destructive techniques for organic extraction such as subcritical water extraction [7]. Although Mars analog locations such as the Atacama Desert show high abundances of perchlorate, it must be considered that Mars surface $[\text{ClO}_4^-]$ are approximately two orders of magnitude greater than terrestrial locations and these catalytic effects during TV would be more pronounced.

References: [1] Hecht M. et al. (2009) *Science*, in press. [2] Navarro-González R. et al. (2009) *Geophys. Res. Abs.*, 11, 1549. [3] Ericksen G. E. (1981) *USGS Prof. Pap.*, 1188, p37. [4] Bao H. and Gu B. (2004) *Environ. Sci. Technol.*, 38, 5073-5077. [5] Navarro-González R. et al. (2003) *Science*, 302, 1018-1021. [6] Aubrey A. D. et al. (2008) *Astrobiology*, 8, 583-595. [7] Amashukeli X. et al. (2007) *JGR*, 112, G04S16.

THE ROLE OF AQUEOUS ALTERATION IN THE FORMATION OF MARTIAN SOILS J. L. Bandfield¹, A. D. Rogers², and C. S. Edwards³. ¹Department of Earth and Space Sciences, University of Washington, Seattle (joshband[at]u.washington.edu). ²Department of Geosciences, Stony Brook University, NY. ³School of Earth and Space Exploration, Arizona State University, Tempe.

A major focus of martian exploration is to understand how much and under what conditions liquid water has been present throughout martian history. Elemental composition and mineralogy can give a positive indication of the presence of liquid water at the time of formation. Compositional trends are also indicative of alteration under specific conditions and both orbital and in situ observations have provided an increasingly detailed picture of properties such as the pH and abundance of water present [e.g. 1-3]. Despite the evidence for aqueous processes at many martian locations, martian equatorial dark regions (Surface Type 1 of [4]) have been interpreted as dominated by unweathered materials that have not been significantly altered from the source material. The suite of minerals is consistent with a basaltic composition and there was no need to invoke additional processes to explain the origin of these materials.

We have begun to question this result based on detailed observations from a variety of datasets [5-6]. Both local and global observations indicate a link between source rocks and dark soils on Mars. Locally derived dark soils have a mineralogy distinct from that of proximal rocky surfaces; most notably a lower olivine content (Fig. 1). This pattern is common for many surfaces across the planet. Detailed measurements at the Gusev Plains indicate a similar mineralogical relationship. However, APXS results [7] do not show elemental abundances consistent with significant mineralogical differences (except in S content) between rocks and dark soils (Fig. 2). This apparent disparity can be explained by “cation conservative” weathering. This process can significantly alter the mineralogy of a surface, but water is limited enough to prevent significant transportation of cations away from the source rock. The elemental and mineralogical relationships between rocks and soils appears to indicate that aqueous alteration is an important process in the formation of the martian dark soils that cover much of equatorial Mars.

References: [1] Hurowitz, J.A. et al. (2006) *JGR*, 111, 10.1029/2005JE002515. [2] Poulet, F. et al. (2005) *Nature*, 438, 623-627. [3] Ming, D.W. et al. (2006) *JGR*, 111, 10.1029/2005JE002560. [4] Bandfield, J.L. et al. (2000) *Science*, 287, 1626-1630. [5] Bandfield, J.L. and A.D. Rogers (2008) *Geology*, 36, 10.1130/G24724A.1. [6] Rogers, A.D. et al. (2009) *Icarus*, 200, 10.1016/j.icarus.2008.11.026. [7] Rieder, R. et al. (2004) *Science*, 306, 1746-1749.

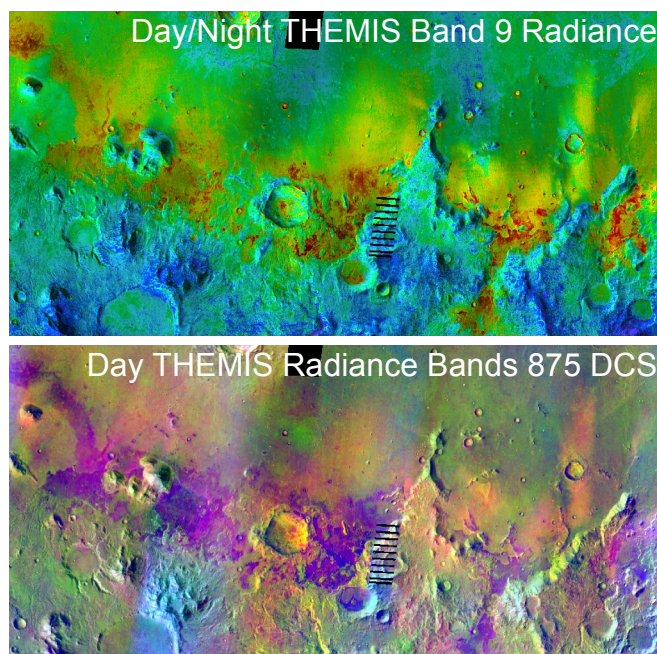


Figure 1. THEMIS mosaics within the southern rim of Isidis Basin, centered near 86E, 4N. The top image shows nighttime radiance in color with daytime radiance for topography. Warmer temperatures (yellow, and red) indicate rockier surfaces. The bottom decorrelation stretch image shows magenta and purple colors that indicate olivine-rich surfaces. Note the correlation of rocky and olivine-rich surfaces. The mosaics are ~300 km across.

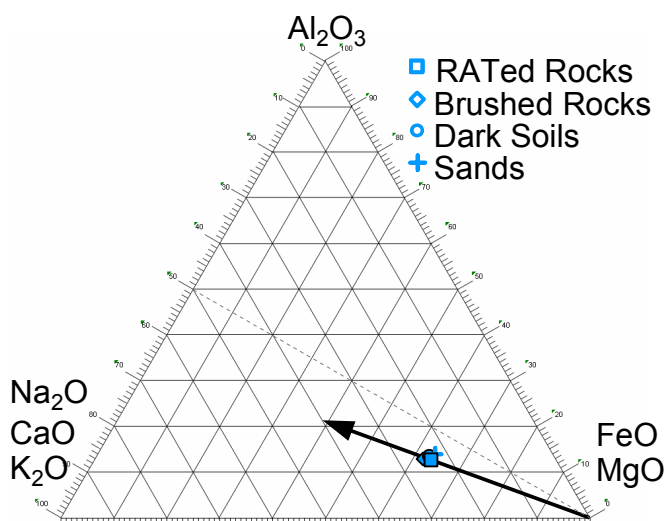


Figure 2. Ternary $\text{FeO}+\text{MgO}$, Al_2O_3 , $\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O}$ diagram (after that of [1]) with the black arrow showing the weathering trend expected under martian conditions. Data are in mole percent from APXS chemistry [7] and are averages of rocks and dark soils within the Gusev Plains. The chemical composition of the different materials are similar despite significant differences in mineralogy indicated by mini-TES and Mössbauer measurements.

ISOTOPIC ANALYSIS OF SALTS IN TERRESTRIAL HYPER-ARID DESERTS: ANALOGS FOR UNDERSTANDING THE ORIGIN AND MOBILITY OF SALTS ON MARS

Huiming Bao, ¹Department of Geology & Geophysics, E235 Howe-Russell Complex, Louisiana State University, Baton Rouge, LA 70803, USA (bao@lsu.edu).

Introduction: The hyper-arid Atacama Desert and the McMurdo Dry Valleys (MDV) are excellent analog sites for understanding the origins and mobility of salts on Mars. Our group has been examining diverse soluble salts (e.g. SO_4^{2-} , NO_3^- , Cl^- , and ClO_4^-), particularly their multiple stable isotope compositions from terrestrial hyperarid surfaces. Past isotope analyses have revealed the sources of sulfate and examined translocation of salts in soils in the McMurdo Dry Valley's, as well as assessed the origin of perchlorate in the Atacama Desert. Aspects of this work should be further explored in light of recent results from the MER rovers and from the Phoenix Mars Lander.

Sulfate Sources: The sulfur and oxygen isotope compositions can reveal the origin of sulfate. The heterogeneity among oxygen and sulfur isotope compositions for sulfates on Earth attests to a dynamic and biologically active planet. The application of three isotope parameters, the $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$, has enabled quantitative determinations of the fractions of three sulfate end-members in soils of the McMurdo Dry Valleys (MDV) [1]. These results show a variable distribution of three end members in different microclimate zones of the valleys, revealing rich information on the fluxes and deposition of sulfate and their history. The apportionment is possible because the absence or near-absence of post-depositional sulfate reduction and because of a new parameter, the $\Delta^{17}\text{O}(\text{SO}_4)$.

Sulfate is known to be present in large quantity in Martian regolith. The sulfate budget on Mars may have two additional constraints, the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, that the Earth does not possess for modern surface environments. Thus, five potential parameters provide much better constraints on individual sulfate end-members when dealing with an inherently underdetermined system such as the mixture of *N* sulfate end-members on Mars.

Leaching Behavior: Similar to Mars, the MDV possesses surfaces where the normally rejuvenating actions of life, water, or ice are limiting. However, aeolian or atmospheric dust/salt accumulation and subsequent vertical migration are on-going processes that have not only altered the physical-chemical nature of the hyperarid surfaces but also recorded past environmental fluctuations during the hyperarid period. We have observed distinct leaching behavior

that is recorded not only by vertical soluble ion concentration profiles but also by the sulfate, nitrate, and chlorine isotope compositions [1,2].

Interpretation of hyperarid soil salt profiles has been contentious, and existing solute transport models for arid soil columns do not apply to the MDV where it is not only extremely dry but also extremely cold. It poses a series of questions on the ability of ion transport by brine at extremely low temperature. Correctly modeling these profiles is important, as their interpretation has significant consequences on our understanding of both MDV and Martian surface histories. Preliminary modeling has qualitatively reproduced the observed concentration profiles by treating ion transport as a function of both the magnitude and the frequency of wetting events.

Perchlorate Puzzle: Perchlorate (ClO_4^-) is a minor component of the hyperarid Atacama Desert salts, and its origin has long been a subject of speculation. Our study has firmly established its atmospheric origin [3]. The evidence came from the measurement of triple-oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) of both man-made perchlorate from commercial sources and natural perchlorate extracted from the Atacama soils. Only the Atacama perchlorate bears an ^{17}O anomaly. However, the small data set exhibits two intriguing observations that demand further study: (1) Both the $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$ for the Atacama perchlorate is rather negative, hinting a fundamentally different photochemical pathway(s) from that of atmospheric nitrate (NO_3^-), and (2) the positive ^{17}O anomalies are variable (from +4.2 to +9.6‰). These results indicate a deficiency in the understanding of Cl cycle and demands the investigation of the unknown alteration process.

While perchlorate is easily detectable in soil of the Central Depression (the driest part of the Atacama Desert), its presence in the MDV soils is curiously low or undetectable. Perchlorate was detected by the Phoenix Mars Lander on Martian regolith. Understanding perchlorate's origin in hyperarid surfaces on Earth should provide the best clue for its origin on Mars.

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THE OUT-GASSING OF A BASALT FLOW AS A SOURCE OF MARTIAN PHYLLOSILICATE. G. Berger¹ and A. Meunier², ¹LMTG, CNRS-Université Toulouse, 14 av. E. Belin, 31400 Toulouse, France, berger@lmtg.obs-mip.fr, ²HYDRASA, University of Poitiers, 40 av. Recteur Pineau 86022 Poitiers, France.

Introduction: Geomorphological observations of Mars surface and mineral detection, in particular hydrated sulphates, militate for the idea that liquid water have existed on Mars surface, even if physical conditions forbid its presence today. Beside the sulphate formation which requires particular chemical conditions, clay minerals are of particular interest because they are the first by-product of aqueous alteration of silicate rocks. Martian clays have been directly observed as iddingsite in SNC Martian meteorites [1], and Fe-Mg clays were spectroscopically detected on the surface of Mars by OMEGA [2].

Basically, clays are produced on the Earth by two contrasted mechanisms: bio-mediated alteration of silicate bedrocks by pedogenetic processes or hydrothermal abiotic thermoactivated alteration. The former being speculative in the Mars context, we focused on hydrothermal processes that could happen on Mars and affect volumes of rocks sufficiently important to be detected by remote sensing techniques.

Modeling: We tested the assumption of Fe-Mg clays formation during magma degassing by analysing terrestrial analogues in the Parana flood basalt province (Brazil). The petrographical and mineralogical characteristics of clay deposits in the prismatic joints of a lava flow [3] are interpreted here using quantitative chemical and thermodynamical models simulating the basalt interaction with Cl₂ rich volatiles. We reproduced an early acidic and oxidizing alteration of the lava flow by out-degassing of H₂O-Cl₂ fluids with disproportionation reactions, followed by a later more conventional alteration by neutral or alkaline evolved hydrothermal solutions. The above alteration model is supported by the mineralogical observations that clearly evidence two different reaction sequences, within the basalt columns or within the inter-columnar joints.

Conclusion: The degassing pathways, by contrast with local hydrothermal systems, can affect large areas (several tens of square kilometres) as it is the case in Mars sites described by [2].

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DISTRIBUTION AND VARIABILITY OF PHYLLOSILICATES ON MARS OBSERVED BY MRO/CRISM AND WHAT THEY CAN TELL US ABOUT EARLY MARTIAN CHEMISTRY.

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Introduction: Abundant phyllosilicate-bearing rocks have been identified across the planet using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on MRO [1]. One region with ample phyllosilicate outcrops is the Noachian-aged upland terrains near the ancient outflow channel Mawrth Vallis; a common phyllosilicate stratigraphy is observed here with nontronite at the bottom, covered by a ferrous phase, with hydrated silica, montmorillonite and kaolinite on top [2]. A similar clay profile is observed in smaller outcrops across a region up to 10⁶ km² [3]. Another region, Nili Fossae, is located west of the large Isidis Basin and contains large outcrops of multiple phyllosilicate minerals [1] and also carbonates [4]. Phyllosilicates were identified previously at these sites via analyses of the Mars Express/OMEGA images [5,6]. Smaller phyllosilicate outcrops also occur across the planet where they are exposed in ancient rocks, often associated with craters [7, 8, 9, 10]. We will present the types, distribution, and environments of phyllosilicates detected on Mars by CRISM.

Phyllosilicates at Mawrth Vallis: Analysis of CRISM images has shown thick profiles of phyllosilicates at Mawrth Vallis that are consistent with long-term aqueous activity and active chemistry. Example spectra from Mawrth Vallis are shown in Figure 1 from 0.4-2.7 μm . Fe/Mg-smectite or nontronite is found as a thick deposit throughout the Mawrth Vallis region. Thinner units of Al-phyllosilicates (montmorillonite, kaolinite, beidellite) and hydrated silica are found above that. Mineral identification is performed using spectral features near 1.4, 1.9, and 2.2-2.4 μm .

Implications for Martian Chemistry. The ancient phyllosilicates in places such as this could have served as reaction centers for organic molecules [11]. Some experiments even suggest that phyllosilicates could have played a role in the origin of life [12]. Regardless of whether life formed on early Mars or not, evaluation of the type and thickness of clay-bearing units on Mars provides insights into plausible aqueous processes and chemical conditions not only during the time of formation of the phyllosilicates, but also the period following their formation.

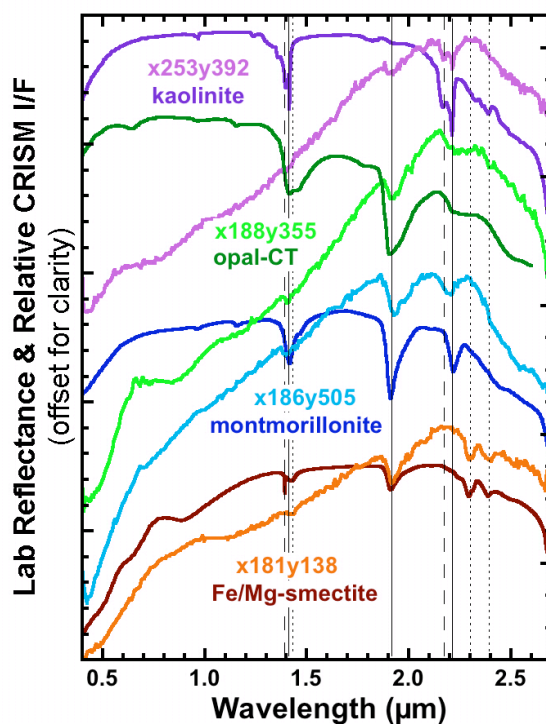


Figure 1. Ratiod CRISM spectra from Mawrth Vallis compared to lab spectra of minerals. Vertical lines are marked to indicate spectral features: solid lines at 1.41, 1.92, 2.21 μm (montmorillonite); dashed lines at 1.38 and 2.17 μm (kaolinite doublets distinct from montmorillonite), dotted lines at 1.42, 2.30, 2.39 μm (Fe/Mg-smectite).

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IN SITU ANALYSIS OF HYDROUS AND AQUEOUS MINERALS USING THE CHEMIN MINERALOGICAL INSTRUMENT ON MARS SCIENCE LABORATORY. D. F. Blake¹, D. L. Bish², S. J. Chipera³, D. T. Vaniman⁴, P. Sarrazin⁵ and the CheMin Team. ¹MS 239-4, NASA Ames Research Center, Moffett Field, CA 94035 dblake@mail.arc.nasa.gov; ²Dept. of Geological Sciences, Indiana University, 1001 East Tenth St., Bloomington, IN 47405; ³Chesapeake Energy Corporation, 6100 N. Western Ave., Oklahoma City, OK 73118; ⁴EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 86545; ⁵InXitu, Inc., 2551 Casey Ave., Suite A, Mountain View, CA 94043.

Introduction: The CheMin mineralogical instrument on Mars Science Laboratory (MSL '09) [1] will return quantitative X-ray diffraction data (XRD) and qualitative X-ray fluorescence data (XRF; $14 < Z < 92$) from scooped soil samples and drilled rock powders collected from the Mars surface. Samples of 45–65 mm³ from material sieved to $< 150 \mu\text{m}$ will be delivered through a funnel to one of 27 reuseable sample cells (five additional cells on the sample wheel contain diffraction or fluorescence standards). Sample cells are 8-mm diameter discs with 7- μm thick Mylar or Kapton windows spaced 170 μm apart. Within this volume, the sample is shaken by piezoelectric vibration at sonic frequencies, causing the powder to flow past a narrow, collimated X-ray beam in random orientations over the course of an analysis.

For typical well-ordered minerals, CheMin has a Minimum Detection Limit (MDL) of $< 3\%$ by mass, an accuracy of better than 15% and a precision of better than 10% for phases present in concentrations $> 4\times$ MDL (12%). CheMin utilizes a Co X-ray tube so that absorption in iron-rich samples is minimized. The resolution of the diffraction patterns is $0.30^\circ 2\theta$, and the angular measurement range is $4\text{--}55^\circ 2\theta$.

Terrestrial Versions of CheMin: Several terrestrial prototype CheMin instruments have been developed to evaluate the capability of the instrument for qualitative and quantitative analysis of single minerals and complex mixtures. Successful Rietveld analyses have been performed using data collected for only 5–10 minutes using the field-deployable Terra instrument, a commercial version of CheMin [2].

Analysis of hydrous and aqueous minerals with CheMin: To date, hundreds of analyses of a wide variety of rocks and minerals have been conducted using Terra and CheMin IV, a laboratory prototype of the MSL CheMin instrument. Some classes of minerals pertinent to the activity of water on the Mars surface are described below:

Analysis of Hydrous Phyllosilicates: OMEGA and CRISM have identified a diversity of hydrous phyllosilicate minerals [3–8]. CheMin can identify and readily distinguish between many of these. Discrimination between 1:1 phyllosilicates (such as the kaolin minerals), with repeat distances of $\sim 7\text{\AA}$, and smectites (e.g., montmorillonite, nontronite, saponite), with re-

peat distances from 10–15 \AA , is straightforward. However, the variety of treatments used in terrestrial laboratories to aid in discrimination of clay minerals will not be accessible on Mars. Geologic context and elemental chemistry should help in this regard. In addition, it should be possible to identify the hydrated kaolin mineral, halloysite. The lowest-angle diffraction peak from 10.1 \AA hydrated halloysite occurs at $\sim 10.2^\circ 2\theta$ with Co radiation and is easily detectable.

Analysis of Carbonates: Carbonates are readily identified by CheMin. The position of the principal peak of the calcite structure can be used to calculate mole % MgCO_3 along the Ca-Mg join. Hydrous phases (e.g., hydromagnesite), ordered phases (e.g., dolomite, ankerite) and orthorhombic phases (e.g., aragonite) can be readily discriminated.

Analysis of hydrous sulfates: Sulfate hydrates identified on Mars include hydrated and anhydrous forms of CaSO_4 (gypsum and anhydrite) as well as various hydration states of MgSO_4 (monohydrates and polyhydrates). Ferric sulfates may play a significant role in producing brines that remain fluid to very low temperatures and the ferric sulfate jarosite has been positively identified, providing evidence of acid-sulfate alteration. All of these phases are readily distinguished by XRD. The nature and hydration states of sulfates will provide important constraints on past and present water-rock interaction on Mars.

Analysis of amorphous silica: Geyserite, Opal A, Opal CT, etc. can be readily distinguished by diffraction. Silica resulting from acid weathering of volcanic materials may be identified by the presence of elements such as Ti in their XRF spectra. Likewise, volcanic glasses have distinct major and minor element signatures in their XRF spectra.

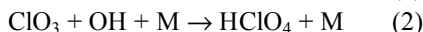
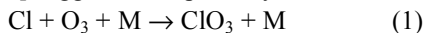
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PERCHLORATE ORIGINS IN THE ATACAMA AND ON MARS. D. C. Catling¹, M. W. Claire², K. J. Zahnle³, R. C. Quinn⁴, B. C. Clark⁵, M. H. Hecht⁶, S. P. Kounaves⁷, ¹Earth and Space Sciences/Astrobiology Program, University of Washington, Box 351310, Seattle WA 98195 (dcating@u.washington.edu). ²Dept. Astronomy/Astrobiology Program, University of Washington. ³NASA Ames Research Center. ⁴SETI Institute/NASA Ames Research Center. ⁵Space Science Institute, Boulder. ⁶JPL/Caltech ⁷Dept. of Chemistry, Tufts University.

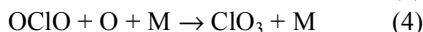
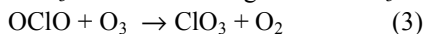
Introduction: Perchlorate comprises ~0.3-0.6wt% of the soil at the site of NASA's Phoenix Mars Lander [1, 2]. Also, on a molar basis, ClO_4^- exceeds Cl^- by about an order of magnitude. But what's its origin?

Hypothetical ways to produce Martian perchlorate include photochemistry, electrostatic discharge, and gas-solid reactions [3]. We propose that the Martian environment especially favors perchlorate production associated with atmospheric oxidants. If so, ClO_4^- could act as a tracer of past volcanic chlorine and its measurement might be fruitful in returned samples [4] or polar deposits drillcores [5]. However, even on Earth, the exact pathway to produce natural perchlorate is unknown. Consequently, we examine perchlorate formation in the Atacama desert to shed light on Mars because perchlorate levels are comparable to those on Mars only in the Atacama [6]. Isotopic studies indicate that such perchlorate is produced by oxidation involving atmospheric ozone [7-9]. Such pathways terminate in perchloric acid (HClO_4) [10], which can dry deposit.

Pathways to perchlorate: For the terrestrial atmosphere, [10] suggested the pathway:



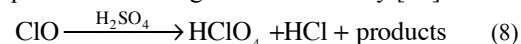
OH reacts with many species, so (2) relies on enough available ClO_3 . OCIO can also generate ClO_3 via [11]:



where OCIO derives from gas-ice interaction [12] or gas phase chemistry. [13] made another proposal with weakly bound ClO.O_2 and ClO.O_3 intermediates:



But ClO.O_3 is hypothetical while the stability of ClO.O_2 remains questionable [14, 15]. A third model postulates heterogeneous chemistry [16]:



However, measurements have shown that ClO uptake on sulfuric acid is insignificantly slow [17].

Method: We examined an Atacama-like atmosphere with a 1-D photochemical model [18, 19]. A flux of HCl was distributed throughout the troposphere to represent a Cl source from volcanism. Model runs had no rainfall and an Atacama-like tropospheric RH.

Results: Fig. 1 shows deposition fluxes as a function of HCl input. ClO_3 is produced predominantly via

(1) and also via (3) and (4); then HClO_4 is produced via (2). Fluxes needed to generate the mass of Atacama salts over the $\sim 10^7$ year age of the deposits are $\sim 10^8$ molecules- $\text{NO}_3/\text{cm}^2/\text{s}$ and $\sim 10^5$ molecules- $\text{ClO}_4/\text{cm}^2/\text{s}$ [3]. Modeled nitrate fluxes compare favorably (Fig. 1). A match for the required perchlorate flux occurs at HCl fluxes 50-60 times higher than estimates of the globally-averaged HCl flux to the atmosphere, $\sim 0.5 \times 10^9$ molecules- $\text{HCl}/\text{cm}^2/\text{s}$ [20]. But a much higher local flux is reasonable given the proximity of the Atacama to Andean volcanoes.

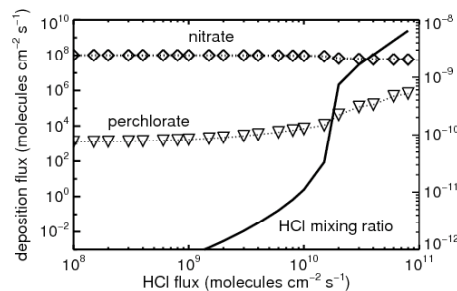


Fig. 1. HCl fluxes (x-axis) result in HCl mixing ratios (solid line) mapped to the R.H. y-axis. Deposition fluxes map to the L.H. y-axis.

Conclusion. We find that the gas phase formation of perchlorate proposed by [10] is feasible for explaining Atacama perchlorate, noting dependence on the uncertain rate of (1). Work is underway with a Mars version of the photochemical model.

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DESERT SOILS AND MARS

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The soils of the hyperarid deserts of Earth are the fundamental analogues for many Mars soils because they have formed in the near absence of life, over time spans up to 10^7 y, and under a very limited availability of liquid water. They are also very geochemically similar to many of the soils examined on Mars [1].

Many attempts have been made to model the geochemical evolution of Martian soils using closed system geochemical models, or one step reactions, with varying results. However, from hyperarid soils on Earth, we know that (1) soil formation is an open system process resulting in chemical and isotopic fractionation during chemical weathering and leaching, (2) climatic boundary conditions undergo large changes over time, resulting in complex weathering histories in any given soil, and (3) these soils nearly always contain incompatible chemical signals of both losses of rock forming elements combined with the later additions of solutes derived from atmospheric deposition and modest downward aqueous redistribution.

An apparent conundrum now exists regarding the spatial variation of Martian soil geochemistry: the vast accumulations of S and Cl in equatorial soils (and the absence or near absence of carbonate) have long been interpreted as indicating an acidic weathering environment, while the recent data from the polar Phoenix lander reveals alkaline pHs and perchlorate. These signals can reflect long term changes in climate and the resulting imprint on old (equatorial) vs young (polar) surfaces. However, there have been no pH measurements made on equatorial soils, and except for the presence of jarosite in distinctive geological deposits, the mineral assemblages provide little direct evidence of acidic conditions. In hyperarid deserts on Earth, soils gradually accumulate S and Cl (from both marine and volcanic sources), have the salts vertically redistributed based on solubility, have neutral pHs, have almost no carbonate due to the low soil CO_2 partial pressures and the competition for Ca by sulfate [2], and can contain considerable quantities perchlorate (as well as nitrates, etc). Thus, the assumed dissimilarities between the Martian soils can also be interpreted, using Earth, as part of a global pedogenic set of processes that have impacted all soils to varying degrees.

A key lesson from hyperarid soils on Earth is the fact that they commonly reflect multiple phases of chemical processes accumulated during climate change. We have shown that using Ti as an index element, that Mars soils at Gusev and Pathfinder sites (like many on Earth) contain evidence of both early stage weathering losses of rock forming elements and late stage additions of atmospheric solutes [1]. While dust influx (and meteorite input in the case of Ni) have been argued as the key source of Martian soils, (1) dust influx into desert soils on Earth invariably leaves a distinctive morphological feature (desert pavement and gravel-free dust below), (2) soils on Mars are apparently chemically weathered relative to reported dust sources, and (3) the use of Ti to normalize soil data reduces the apparent Ni enrichment to much more modest levels (suggesting that some Ni is a weathering residue).

Finally, the source and direction of water movement on Mars is a long source of debate. However, the chemical signature of downward movement of water in Earth soils is a well studied pedogenic and hydrological process. Using this knowledge, shallow soil exposures at Gusev are suggestive of very modest late stage downward movement of water (and redistribution of salts), and the deep exposure at Endurance crater has S, Cl, and Br profiles suggestive of very modest, and late stage, downward movement of water [1,3].

Taken as a whole, there is considerable need to expand the use of, and research on, our most accessible Mars analogue: the soils of Earth.

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THERMODYNAMIC PROPERTIES OF OXIDIZED FORMS OF CHLORIDE AND APPLICATIONS TO THE PHOENIX SURFACE CHEMISTRY. V. F. Chevrier¹, J. Hanley¹, ¹Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, vchevrie@uark.edu.

Introduction: the recent discovery of perchlorates (ClO_4^-) by Phoenix triggered a high interest for this rare ion on the surface of the Earth [1]. Indeed perchlorate solutions have very low eutectic favoring potential liquid water on the surface [2]. The mechanisms by which such a highly oxidized ion formed remain largely unknown. Two major pathways are possible: atmospheric oxidation of aerosols [3], potentially through UV or reaction of strong oxidants like H_2O_2 with chlorides in liquid or solid form. A major problem for these models is the lack of thermodynamic data. Indeed, between chloride (oxidation state -1) and perchlorate (oxidation state +7) three other ions exist: hypochlorite ClO^- (+1), chlorite ClO_2^- (+3) and chlorate ClO_3^- (+5). These ions may be present (and undetected) at the Phoenix landing site as intermediate species of the processes leading to perchlorates.

Therefore, we started a detailed investigation of the thermodynamic properties of the intermediate oxidation states of chloride. Using literature data we determine the thermodynamic parameters controlling their stability, focusing on sodium and magnesium as being the most relevant to the Phoenix chemistry [2,4].

Results and discussion: Table 1 summarizes preliminary data gathered for Na-species from stability diagrams (Fig. 1). All except the chlorate have one or several hydrates, the highest being hypochlorite. We observe a general decrease of eutectic temperature with increasing oxidation of Cl, perchlorate presenting the lowest value.

Table 1. Eutectic conditions determined for the oxidized species of Na. Perchlorates are indicated for comparison.

Specie	Hydrates	Eutectic T	Eutectic C
NaClO	5 and 2.5	257 K	19 wt%
NaClO_2	3	n.d.	n.d.
NaClO_3	-	250 K	39 wt%
NaClO_4	2,1	236 K	52 wt%

For $\text{Mg}(\text{ClO}_x)_2$, the situation is even more complicated since we have only found data for the chlorate (Fig. 2). The measured eutectic is much higher than for perchlorate (255 against 206 K), but interestingly $\text{Mg}(\text{ClO}_3)_2$ presents similar hydration states than $\text{Mg}(\text{ClO}_4)_2$: 6, 4 and 2 H_2O .

These preliminary results show the need for thermodynamic data of aqueous equilibrium and water vapor equilibrium [5]. Using these data we will extract the Pitzer parameters used in the thermodynamic models of perchlorate formation and stability through evaporation and freezing [4].

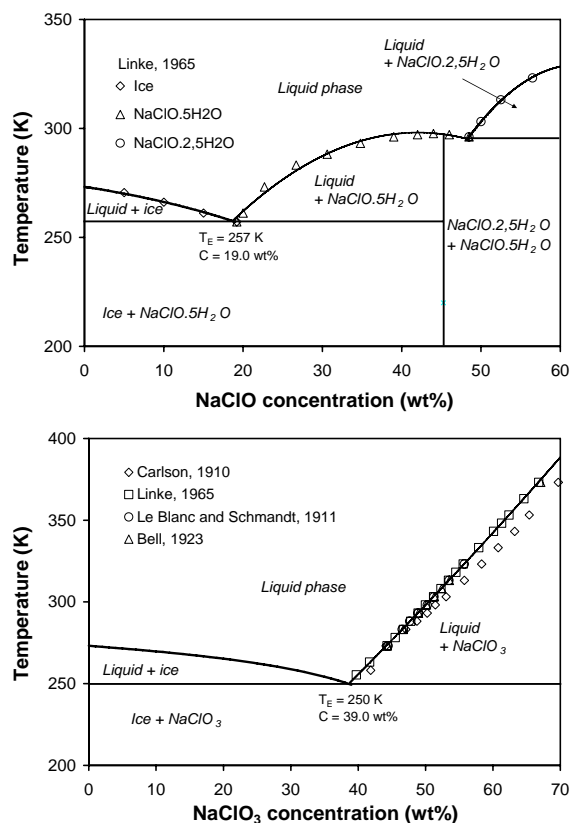


Figure 1. Thermodynamics stability diagrams of sodium hypochlorite (top) and chlorate (bottom).

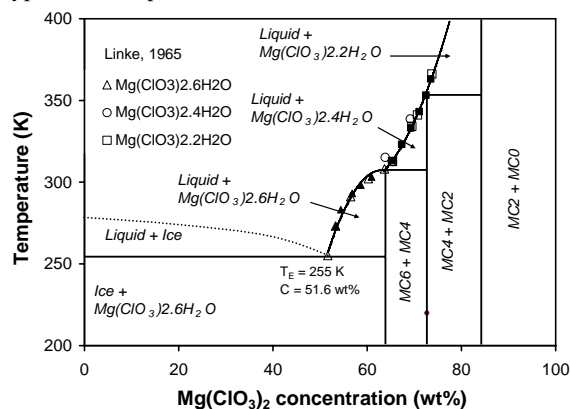


Figure 2. Partial thermodynamic stability diagram of magnesium chlorate. The ice – liquid dotted line needs to be determined.

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PERCHLORATE ON EARTH AND MARS, FORMATION PROCESSES, FATE, IMPLICATIONS FOR ASTROBIOLOGY AND SUGGESTIONS FOR FUTURE WORK. Max Coleman, NASA Astrobiology Institute and Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, M/S 183-301, Pasadena CA 91101. max.coleman@jpl.nasa.gov.

Introduction: The discovery of perchlorate (ClO_4) by the Phoenix mission [1] has posed many questions about its origin and possible effects on the other components of martian surface soils and sediments. This paper reviews the ClO_4 geochemical cycle on Earth and discusses whether these are applicable to Mars and suggests future work to elucidate the issues raised. Much of the research so far has been driven by forensic needs, firstly terrorist bombs but later environmental differentiation of manufactured and natural perchlorate. Most advances used stable isotope approaches that inform all aspects of the subject.

ClO_4 on Earth: The largest concentration of ClO_4 is associated with another oxyanion salt, nitrate, in the Atacama Desert [1]. Its concentration varies between 0.1% and 1% in deposits but local values as high 2 to 3% occur. However, it also occurs at low concentrations in potassium-rich evaporite deposits [2], in vadose zones of soils or sands in the SW states of the USA [3], in atmospheric precipitation [4] and in seawater [5]. Clearly, because of their great solubility both nitrate and perchlorate only accumulate in the arid environments, but how do they get there?

Origin of terrestrial ClO_4 : Cl isotopic analysis of ClO_4 was developed in response to the need to characterize chlorate and ClO_4 in terrorist bombs [6] but it is most powerful coupled with its O triple isotope composition. Mass-independent fractionation of O ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ changed from the normal approx. 1:2 ratio) indicates its origin and formation process. The positive $\Delta^{17}\text{O}$ values for Atacama ClO_4 (and nitrate), are like those of ozone, indicate formation by UV induced reactions of oxygen in the troposphere and stratosphere [8] and possible reaction with seawater aerosol Cl. Accumulation in arid environments arises from particulate deposition, which may occur uniformly over the Earth but is not preserved, potentially implying a considerable flux. In contrast, manufactured ClO_4 , used extensively in propellants for solid-fuel rockets and also for air bags, fireworks and road flares, has isotope compositions showing only mass-dependent O values. Thus, there is a clear isotopic differentiation between natural and manufactured ClO_4 [10]; much of the latter disposed of carelessly, has led to major water resource pollution. Such environmental problems led to much research on microbial degradation of ClO_4 .

Microbial degradation of ClO_4 : Microbes that grow by reducing ClO_4 to chloride [11] occur in many

environments [12] (all are nitrate reducers too). Measuring the associated Cl [13,14] and O [15] isotope fractionations showed very large values used to determine the extent of microbial degradation of pollution. Also, isotopes showed that microbial reduction is currently active in degrading manufactured pollutant ClO_4 in the vadose zone of desert sands in Israel [16], a feasible Mars analog environment. A similar interpretation could be applied but less robustly to the Atacama.

ClO_4 on Mars: Although ClO_4 has been identified only by Phoenix, elemental analyses indicate almost ubiquitous presence of Cl and some or all of it may be perchlorate or other Cl oxyanions. It is unlikely that its mode of formation is like that on Earth, however, it could be formed by surface UV induced reactions with oxidants like iron oxides. It is possible other Cl oxyanions also could be produced. Chlorate, chlorite and hypochlorite react with and destroy organic matter while perchlorate is more stable but most are plausible electron acceptors for microbial respiration processes.

Future work: To address future Mars science needs, possible formation processes must be investigated together with biological and abiological degradation. In all cases it is essential to use isotopic characterization which has been the key to terrestrial understanding and can differentiate biological from inorganic equivalent products. A design for a feasible in situ isotope instrument already exists. All of these will be addressed in detail in the presentation.

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POTENTIAL LIFESTYLES IN ANCIENT ENVIRONMENTS CHARACTERIZED BY THE MARS EXPLORATION ROVERS. D. J. Des Marais¹, ¹Mail Stop 239-4, NASA Ames Research Center, Moffett Field, CA 94035-1000, David.J.DesMarais@nasa.gov

A central goal in Mars exploration is to determine whether life has ever existed there and, whether it did or not, the degree to which the Mars environment could have sustained life. To attain this goal, we can characterize the environmental context, identify places most likely to have sustained life and retained evidence of its presence, and search for “biosignatures,” namely features created only by life and that can persist long after they were formed. Life as we know it requires liquid water, source(s) of energy to sustain metabolism, and chemical building blocks for its cellular constituents. The availability of liquid water appears to be the primary limiting factor in near-surface Martian environments. Liquid water apparently was more widespread on the surface in ancient times and it has occurred within the crust at various times. Oscillations in the orbital obliquity of Mars probably influenced the distribution of water, and some evidence hints of recent liquid water.

Observations by Spirit rover indicate that conditions have probably been too dry to sustain life, at least since the emplacement of the extensive basalts that underlie the plains around the Columbia Memorial Station landing site. Local evidence of relatively minor aqueous alteration probably occurred under conditions where the activity of water was too low to sustain biological processes as we know them.

In contrast, multiple bedrock units in West Spur and Husband Hill in the Columbia Hills have been extensively altered, probably by aqueous processes. The Fe in several of these units has been extensively oxidized, indicating that, in principle, any microbiota present during the aqueous alteration of these rocks could have obtained energy from Fe oxidation. Spirit discovered olivine-rich ultramafic rocks during her descent from Husband Hill southward into Inner Basin. Alteration of similar ultramafic rocks on Earth can yield H₂ that can provide both energy and reducing power for microorganisms. Spirit’s discovery of “salty” soil horizons rich in Fe and/or Mg is consistent with the aqueous dissolution and/or alteration of olivine. Such processes can oxidize Fe and also yield H₂ under appropriate conditions. Very high S concentrations in these salty deposits indicate that soluble salts were mobilized by water and/or that S oxidation, a potential energy source for life, occurred. The Athena team has not yet established whether these salt components were deposited as large beds in ancient water bodies or, for example, were concentrated by more recent groundwater activity. Collectively these observations are consistent with the

possibility that habitable environments existed at least intermittently in the distant geologic past.

MER Opportunity revealed that habitable environments might have persisted for an extended period of time in the Meridiani Planum region at some time in the distant past. If these ancient aqueous environments had been highly acidic, this acidity might have inhibited prebiotic chemical reactions leading to the origins of life at those locations. But we must admit that the attributes of any Martian life might differ in fundamental ways from life on Earth.

We must be prepared to explore a “gray zone” that extends beyond the characteristics or limits of life as inferred from our terrestrial example. The Martian meteorite ALH84001 might be an example of such a “gray zone.” Mars exploration will engender years of continuing analysis, debate and, perhaps eventually, profound insights about the potential for life in the universe.

PROBING MARTIAN SURFACE CHEMISTRY WITH LIBS: MAJOR AND MINOR ELEMENT ANALYSES WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY. M. D. Dyar¹, J. M. Tucker¹, S. M. Clegg², M. W. Schaefer³, R. C. Wiens², J. E. Barefield II². ¹Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, mdyar@mtholyoke.edu, jtucker@mtholyoke.edu, ²Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, sclegg@lanl.gov, rwiens@lanl.gov, jbarefield@lanl.gov, ³Dept. of Geology and Geophysics, E235 Howe-Russell, Louisiana State Univ., Baton Rouge, LA 70803, mws@lsu.edu.

Introduction: LIBS (Laser-Induced Breakdown Spectroscopy) will be used by ChemCam on the Mars Science Laboratory rover for remote elemental identification and quantification in rock and soil samples. LIBS uses a laser pulse focused onto a sample, creating a plasma of excited atoms and ions whose emissions give rise to spectroscopic features characteristic of specific ions and molecules.

Previous work on geological samples [1,2] has focused on quantification of major elemental abundances, e.g. Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti. These elements (with oxygen) typically account for >99% of the mass of the sample. We are currently expanding upon these studies by pursuing quantitative analysis of both minor elements, whose abundances are typically less than a few hundred parts per million [3], and other elements less routinely analyzed in terrestrial rocks such as H, C, S, and O. These elements are important for understanding Martian geochemistry.

However, quantitative elemental analyses using LIBS are possible only when chemical matrix effects, which influence the ratio of a given emission line to the abundance of the element producing that line, are considered. We present here a progress report from a multi-faceted study of methods for multi-element analysis of igneous rock types using LIBS.

Experimental: Samples for this study are the same as those used in [2], plus an additional 100 igneous samples with wide-ranging compositions. All samples were analyzed for major and minor elements in Michael Rhodes' XRF lab at the Univ. of Massachusetts using standard operating procedures [4] for internally-consistent results. H, S, and C were analyzed in the lab of Zach Sharp at UNM, where wt% H₂O is measured by reducing the samples at high temperatures with graphite, and the other elements are measured using an elemental analyzer.

The LIBS experimental conditions are chosen to mimic ChemCam operating conditions as closely as possible. Samples were placed in a vacuum chamber filled with 7 Torr CO₂. An Nd:YAG laser pulsing at 10 Hz produces the LIBS plasma. Spectra were obtained using three Ocean Optics HR2000 spectrometers covering the spectral ranges 223-326 nm (UV), 382-471 nm (VIS), and 495-927 nm (VNIR).

Results: We are exploring factors that affect the success of univariate and multivariate calibration techniques. For both methods, it is apparent that use of background-subtracted spectra for statistical analyses will produce superior quantitative results. We are also currently comparing results of analyses using two different types of input: channel intensities vs. peak areas.

Multivariate methods are complicated by elemental correlations, both positive and negative, that arise from fundamental elemental substitutions. Because of this, it is important to make sure that predicted elemental abundances are substantially based on the emission lines of the element of interest and not simply on geochemically-related elements [3].

Partial Least Squares (PLS) methods for interpretation of LIBS spectra show great improvement over univariate methods [2]. Careful selection of samples used to build PLS models and attention to the compositional ranges they represent are critical to successful prediction of elemental abundances in unknown samples. PLS-2 results also highlight the influence that disparate concentration ranges can have on a regression model, and suggest that a key to obtaining good analyses for minor elements is normalization/rescaling of concentrations before input into statistical models.

PLS is only one of many multivariate regression techniques that could be used for calibration. Other techniques that explicitly take the issue of multicollinearity into account are also currently under investigation, such as forward and stepwise regressions. It is now clear that the LIBS technique has the capability to produce robust, quantitative analyses *not only* for major elements, but also for a large range of light elements and trace elements that are of great interest to geochemists. This list includes at least H, B, C, N, O, Be, Li, V, Cr, Ni, Sr, Zr, and Ba (in addition to major elements). ChemCam results from MSL should thus complement and expand upon those from the MERs and the Phoenix lander.

Acknowledgments: We are grateful for support from MFRP grant # NNG06GH35G.

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REGIONAL CARBONATE- AND KAOLINITE-BEARING ROCK UNITS AND HOW PRECURSOR LITHOLOGIES CONTROL ALTERATION PRODUCTS ON MARS: AN EXAMPLE FROM THE NILI FOSSAE REGION. B. L. Ehlmann¹, J. F. Mustard¹, and the CRISM Team. ¹Department of Geological Sciences, Brown University, Providence, RI 02912 USA (bethany_ehlmann@brown.edu)

Alkaline soil chemistries revealed by Phoenix lander investigations [1] and smectite clays discovered by the OMEGA instrument on Mars Express [2-4] suggest neutral to alkaline aqueous alteration has been important on Mars in both the Amazonian and Noachian epochs, in contrast to dominantly acidic conditions indicated at both MER landing sites. The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard the Mars Reconnaissance Orbiter has discovered additional phases resulting from near-neutral/alkaline pH aqueous alteration—diverse hydrated silicates (chlorite, serpentine, illite/muscovite, kaolinite), prehnite, magnesium carbonate, and zeolites [5-7]. Here we describe regional kaolinite- and carbonate-bearing rock units found in Noachian terrain near Nili Fossae and hypotheses for their formation.

Stratigraphy: The kaolinite- and carbonate-bearing rock units are at most a few 10s of meters thick and show no bedding at HiRISE (25 cm/pixel) resolution. Both units occupy a similar stratigraphic position above a brecciated unit of Fe/Mg smectite and unaltered mafic silicates, interpreted to be ejecta and fallback from the Isidis impact [8]. In many cases, the kaolinite- and carbonate-bearing units are overlain by a mafic cap rock that shows no evidence for alteration minerals. There is a clear geographic zoning of kaolinite vs. carbonate, with the latter prevalent in the eastern portion of the Nili Fossae region, associated with a thin, regional unit enriched in olivine [6,8] (Fig. 1).

Timing: Both units definitely post-date the Isidis impact (i.e. formation mid-Noachian or later) [9]; however, both are also cut by the fossae. This indicates that at least some of the alteration occurred prior to the fossae opening, which probably occurred in the Late Noachian [10].

Formation mechanisms: As discussed in [6,8], the Mg carbonate (and also serpentine [7]), probably represents localized, partial alteration of a mostly unaltered regional olivine-rich rock unit [8]. Carbonate, serpentine, and olivine are found in laterally varying zones which show no distinctive morphologic change to coincide with the changes in unit spectral properties. One possibility for the formation of carbonate and serpentine in olivine-rich rocks is hydrothermal activity under elevated $p\text{CO}_2$. Emplacement of hot olivine-rich rocks as Isidis impact melt or volcanic flows on top of water-bearing phyllosilicate rocks may have initiated hydrothermal alteration in a zone along the contact. An alternative explanation is surface weathering. Mg car-

bonates are observed weathering products for olivine-rich meteorites in Antarctica [11] and terrestrial serpentinite bodies [12].

Where olivine is not detected in VNIR spectral observations, carbonate is also not detected. Kaolinite is frequently found above smectites and beneath the mafic cap. Kaolinite can form hydrothermally, though the spectrally distinct high-temperature polymorphs dickite and nacrite are not observed. Another plausible formation mechanism is pedogenic-type leaching of pre-existing smectite-bearing deposits, leading to loss of Ca, Mg, and Fe ions and precipitation of kaolinite, as in formation of kaolin-bearing soils from basalts in Hawaii [13]. Ongoing investigation of the *in-situ* bedrock and intact stratigraphy of the kaolinite- and carbonate-bearing rocks here should permit determination of constraints on the timing and processes of neutral/alkaline aqueous alteration on Mars.

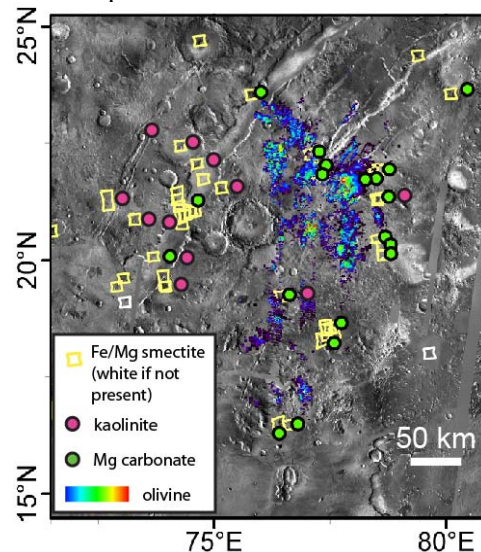


Figure 1. Distribution of kaolinite (magenta dots), magnesium carbonate (green dots), and Fe/Mg smectites (orange outlines) identified in CRISM targeted data in relation to mafic rocks with olivine spectral signatures around the Nili Fossae, mapped using OMEGA data as in [6].

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WATSEN – A MID-IR SPECTROMETER, HUMIDITY SENSOR AND OPTICAL MICROSCOPE TO IDENTIFY THE SUBSURFACE WATER AND MINERALOGY OF MARS.

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Introduction: Mars is currently the main focus of extra-terrestrial planetary investigation in terms of the number of surface and orbital instruments deployed there. Although several missions have scratched into the surface (most recently Phoenix) there have not been deeper measurements of the martian subsurface. Phoenix has discovered the surrounding soil to be comparable to soils found in Antarctica's Dry Valleys [1]. It seems clear from the initial results that the soil is pH alkaline (8.3 ± 0.5) [2] and that water has been involved in the formation of the soil, detected in the form of subliming ice [3]. The presence of CaCO_3 and soluble ionic species detected by TEGA and MECA [4,2] further suggests the presence of water interacting with soil at some point. Since conditions at the martian surface are unfavourable for the presence of water and potential organic signatures [5] it is necessary to look deeper into the subsurface. Recent classification of geological eras [6] suggests an early warm and wet martian environment in which phyllosilicates formed (called the Phyllosian era). Nili Fossae [7] is a region that the orbital VNIR and IR spectrometers OMEGA and CRISM [8,9] have indentified which correspond mineralogically and through crater counts to this early Phyllosian era. This location would be a prime candidate for the detection of Mars' fluvial past, with phyllosilicates detected and CRISM indentifying MgCO_3 [10] (known to be abundant in the presence of water, CO_2 and an alkaline pH; all conditions hospitable for most terrestrial life).

WATSEN: So were those early conditions warm and wet and potentially favourable to life? Hopefully these questions will be answered by looking into the martian regolith with *WatSen*, a miniaturized instrument consisting of a combined Attenuated Total Reflectance (ATR) IR spectrometer, optical microscope and humidity sensor. *WatSen* is designed to be part of a suite of instruments onboard a mole on a planetary lander similar to ExoMars. A burrowing mole would allow *WatSen* to make multiple readings at intervals of depth providing an insight into mineral variation, humidity, water presence and perhaps biological activity. As part of a mole, *WatSen* could penetrate down to 5 m in depth. These would be the first measurements of the non-oxidised subsurface and may be below the zone of sublimation [11]. The ATR sensor operates by measuring the changes that occur to the totally internally reflected infrared beam upon contact with the sample. Surface properties alter the spectral reflectance in a mineral grain, thus the ATR

has a flat surface in intimate contact with the sampling surface [12]. The optical microscope will aid mineral identification with images of the grains in contact with the ATR being generated at each spectral location. The humidity sensor will continually detect any water present in the bore hole during *WatSen*'s descent, whether it is in the form of vapour subliming or direct contact with liquid water [11].

Spectral studies: Showed that soil components typical of Mars will be uniquely identifiable within the chosen wavelength range (5.5 - 10.8 μm) [12]. This wavelength range is a trade off between technical boundaries and the ideal wavelengths; H_2O absorption is stronger at 3 μm , but strong and distinct absorption peaks for minerals occur in the mid infrared spectrum (5 - 11 μm). An example is carbonate minerals, which have recently been identified by CRISM's orbital reflectance spectral data and through direct surface analysis, in the mid-infrared these carbonates display a unique spectral shape between 6.3 - 7.4 μm . Water IR spectral features are also displayed between 6 - 7 μm , but major features of anhydrous silicates occur at wavelengths greater than 9 μm . Furthermore, hydrated minerals such as clays display combined features of water and silicates. *WatSen*'s 0.015 $\Delta\lambda/\lambda$ resolution is sufficient to resolve distinct spectral features for water and minerals found on Mars.

Implications: As the surface of Mars is constantly weathered by the planet-wide dust storms that spread and mix the loose surface soil components it is the layered subsoil material that will reveal Mars' past history. In addition the surface oxidizing solar radiation makes conditions inhospitable, for life but beneath the surface in briny solutions this may not be the case. Rather than merely scratching the surface a penetrating mole would supersede its martian predecessors and with *WatSen*'s instruments would help characterize the past climate of Mars.

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HYDROUS PERCHLORATES AND THEIR RELATION TO HUMIDITY AT THE PHOENIX LANDING SITE.

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Introduction: Phoenix showed the presence of ~1% perchlorate in the landing site regolith [1]. This ion is associated to sodium and magnesium [2], making these compounds ideal candidates for liquid brines on the surface. In addition, hydration-dehydration cycles may control the humidity. We study the stability of perchlorates (liquids and salts) under Martian conditions using a combination of experiments and models, which is then applied to Phoenix observations [3].

The previously determined phase diagrams [3] for NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$ show that the eutectic temperature is 236 K for 52 wt% NaClO_4 and 206 K for 44 wt% $\text{Mg}(\text{ClO}_4)_2$. Using a combination of thermodynamic (Pitzer) and water evaporation kinetic models [3], we calculated evaporation rates for the Phoenix landing site conditions.

Liquid Stability: While temperatures are more favorable for liquid solutions on the warmest day, equilibrium vapor pressure values are also higher, so liquid

perchlorate solutions are evaporating (Fig. 1). Paradoxically, on the coldest days, the atmospheric water vapor pressure is above the saturation value of eutectic $\text{Mg}(\text{ClO}_4)_2$ solutions, making the liquid thermodynamically stable for a few hours (Fig. 1A). This is not the case for NaClO_4 where a higher eutectic makes it evaporating or frozen, but never stable.

We obtained the cumulated evaporated thickness over time (Fig. 1B). Although, the main control on the evaporation rate is the temperature, liquid once formed remains metastable for several days.

Humidity Control: Water vapor pressure exhibits strong diurnal changes associated with temperature fluctuations, suggesting coupling with the regolith, such as changes in the hydration state of perchlorates. At low temperatures, $\text{Mg}(\text{ClO}_4)_2$ has only one hydrate: 6 H_2O , which is stable up to 409 K, where it converts to $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ [3]. Although no evidence supports hydration higher than 6 H_2O , we suggest a transition to 5 H_2O at low humidity (Fig. 2).

When looking at the activity of water versus temperature in the soil (Fig. 2), we notice a clear trend along the MP6-MP5 curve. Almost all the values are in the stability field of $\text{Mg}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$. Another boundary is the solidus line, confirming control of humidity by Mg-perchlorates and the presence of liquid brines..

Further investigation into the effects of perchlorate hydration on atmospheric humidity is necessary. The next step will be determining the perchlorates hydration states at low- $p_{\text{H}_2\text{O}}$ and low-T.

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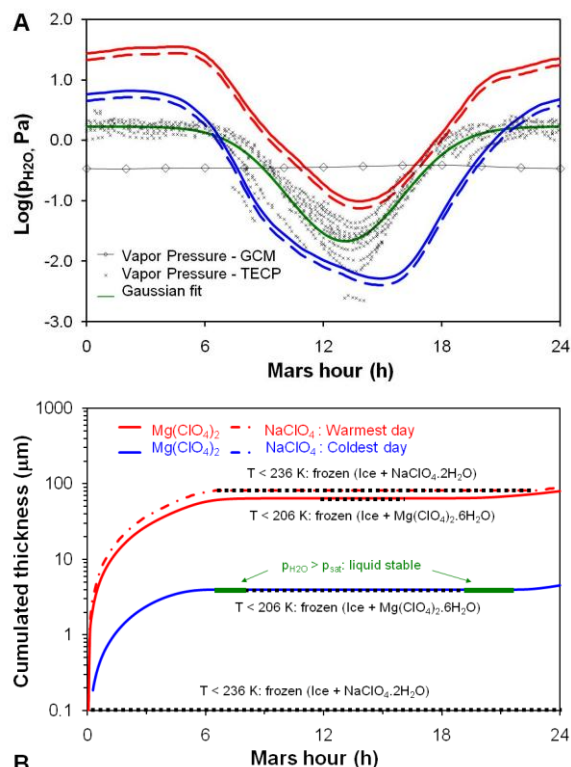


Figure 1. (A) Atmospheric water vapor from TECP (crosses) compared to modelled values from GCM (diamonds) and equilibrium values above eutectic solutions of NaClO_4 (dashed) and $\text{Mg}(\text{ClO}_4)_2$ (plain) for the coldest (blue) and warmest (red) days. (B) Integrated evaporation curves over time after noon for $\text{Mg}(\text{ClO}_4)_2$ and NaClO_4 . Thick dotted black lines represent frozen periods. Green areas represent stable periods for liquid $\text{Mg}(\text{ClO}_4)_2$ eutectic solutions.

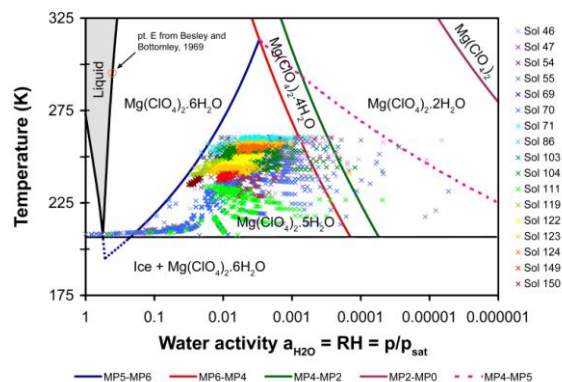


Figure 2. Temperature versus water activity in the soil, plotted with the stability diagram for $\text{Mg}(\text{ClO}_4)_2$. Solid lines are from Besley and Bottomley [4] and data points are from TECP's humidity sensor.

REFLECTANCE SPECTRA OF LOW-TEMPERATURE CHLORIDE AND PERCHLORATE HYDRATES AND THEIR RELEVANCE TO THE MARTIAN SURFACE.

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Introduction: Chlorides and perchlorates present on Mars can form aqueous solutions because of low temperature eutectics and related lower evaporation rates [1]. The recent discovery of chlorides and perchlorates on Mars by NASA's Phoenix Lander [2] reinforced the potential for chlorides on Mars.

Chlorides present in databases lack spectral features (absorption bands) in the near-infrared. Most spectral libraries contain only high temperature "Earth-relevant" chlorides, such as NaCl or KCl. However, at typical Martian relevant temperatures, hydrates are more stable [1]. Similarly, not much is really known about perchlorate spectral features.

Experimental: The following salts and their low-temperature hydrates were synthesized and measured: KCl, NaCl, CaCl_2 , MgCl_2 , FeCl_2 , FeCl_3 , NH_4Cl , NaClO_4 , KClO_4 , and $\text{Mg}(\text{ClO}_4)_2$. We also measured eutectic mixtures of ice and salt. Reflectance spectra were taken using a Nicolet 6700 FTIR Spectrometer to allow analysis in the range 1.0–2.5 μm . For comparison reasons, chlorides and perchlorates stable at ambient temperature were also measured. In the case of eutectic mixtures, we corrected for ice content using KCl + ice as a control sample since it does not form any hydrate.

Results: *Chlorides.* After correcting the spectra for water ice, we see KCl does not exhibit any significant features, nor does anhydrous NaCl (Fig. 1). However, other anhydrous chlorides (e.g. CaCl_2), as well as their hydrated forms, clearly show evidence of additional absorption bands. The most significant bands are located at 1.19, 1.44 and 1.97, the latter two due to hydration. Also, notice that the absorption band depth increases with increasing hydration state.

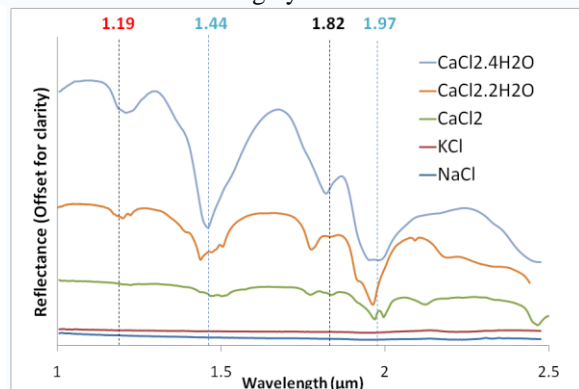


Figure 1. Diffuse reflectance spectra of various Mars-relevant chlorides. Note the presence of spectral features in all hydrated forms, as well as in anhydrous CaCl_2 .

Perchlorates. Perchlorate spectra show numerous absorption bands (Fig. 2). Even anhydrous perchlorates

have significant spectral features, as shown by KClO_4 , which shows major absorption bands at 1.23, 1.55, 2.01 and 2.13 μm (Fig. 2A). $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ shows even more absorption bands (Fig. 2B), although at different positions, except for 2.14 μm (possibly due to the Cl-O bond in the perchlorate ion). Other major bands are located at 1.17, 1.42, 1.46 and 1.93 μm , the latter three corresponding to the usual hydration bands observed in all the hydrated phases. We do not observe any significant spectral difference between $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ except an increase in band depth due to the higher water content.

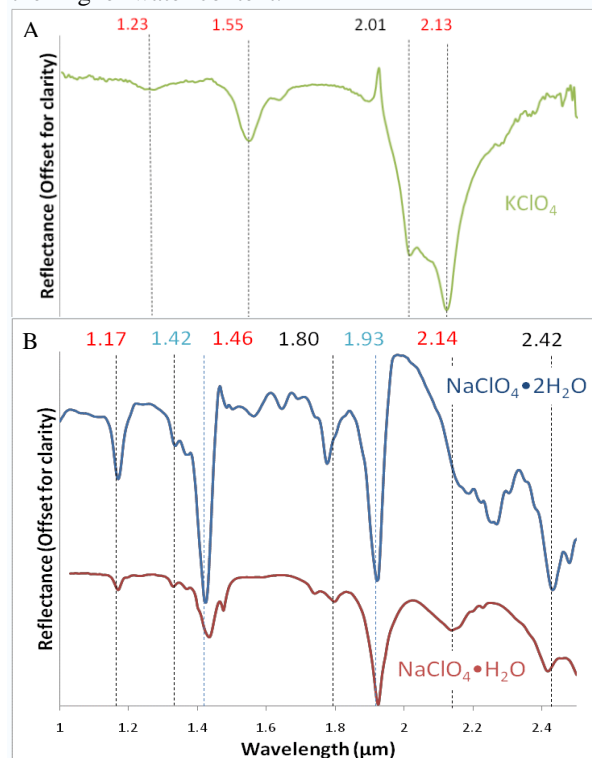


Figure 2. Diffuse reflectance spectra of (A) KClO_4 and (B) NaClO_4 hydrates.

Conclusions: Chlorides and perchlorates show significant spectral features that should allow for their identification on the surface of Mars: perchlorate bands are present at ~1.2, ~1.5, & 2.11–2.14 μm ; hydrates show bands characteristic of hydrated phases (1.4 and 1.9 μm); and hydration band depth increases with increasing hydration state. Therefore, some unidentified hydrates could be chlorides or perchlorates.

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INTRODUCTION TO NEW MARTIAN CHEMISTRY WORKSHOP: "FOLLOW THE CHEMISTRY"

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In the post-Viking era, Mars was defined largely in terms of geomorphology and the planet-wide cycles of water, dust, and CO₂. In the 21st century, we have increasingly come to understand Mars in terms of chemical processes. Soil chemistry has become a key to understanding geological, astrobiological, and even atmospheric processes. What the future holds for our understanding of Mars will be determined by NASA's Decadal Survey and similar European strategic planning endeavors. It is suggested here that a high priority for future exploration should be assigned to *in situ* and orbital studies of the chemical diversity of present-day martian soil and, where stratigraphy allows, the historical record of that chemistry.

The **mineralogy** story unfolded largely from orbit. In 2002, for example, data from the Gamma Ray Spectrometer suite was interpreted to be indicative of reservoirs of hydrated minerals at low latitudes [1]. Hints of hematite from the THEMIS instrument [2] ultimately led to the *in situ* discovery of "blueberries," putative aqueous concretions captured by MER's microscopic imager [3]. In 2006, drawing from measurements by the OMEGA instrument, Bibring et al [4] suggested that the martian epochs previously defined morphologically as Noachian, Hesperian, and Amazonian might more suggestively be defined as the ages of clays (Phyllosian), sulfates (Theiikian), and anhydrous ferric oxides (Siderikian), referring to the products of nonacidic aqueous alteration, acidic aqueous alteration, and aqueous-free oxidation respectively.

The **soil science** story is currently emerging, with the Phoenix mission providing notable contributions. Martian soil from one (subpolar) site has proven to be near-neutral in pH, buffered by calcium and possibly magnesium carbonates; laced with highly oxidized chlorine in the form of perchlorate; and may contain a modest fraction of sulfates, probably in the form of calcium sulfate [5,6]. The presence of perchlorate, in particular, suggests that photochemistry plays an important role in soil chemistry, and also implies that low temperature aqueous processes may be occurring in brines even today. The microscopic particle size distribution determined by the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) on Phoenix argues against extensive chemical modification of the soil, while atmospheric humidity measurements, when compared to soil temperature measurements, suggest that the "breathing" of salts in the soil may actually regulate the atmospheric water content.

Astrobiology and chemistry are linked both through models of possible biological evolution on

Mars and through strategies for seeking evidence of such life. The Viking biology experiments inspired speculations that oxidizing soil chemistry may be inimical to the survival of the simplest prebiotic molecules [7,8]. Tosca et al. [9] extended that idea, suggesting that mineralogical evidence implied an early, aqueous Mars too acidic and saline to support the development of microbial life as we know it. From the perspective of searching for life, Capone et al [10] recently suggested that "follow the carbon" may not be the best strategy. While the carbon cycle may dominate biology, the reverse is not true. The nitrogen cycle, on the other hand (and particularly the denitrification process) is strongly influenced by biology, and the lack of nitrogen in the martian atmosphere may in and of itself contra-indicate life. In light of Phoenix findings, it might similarly be argued that dechlorination is predominantly a biological process, and the presence of large quantities of perchlorate may therefore contra-indicate extant biology.

On a predominantly dry planet, the influence of **atmospheric chemistry** is relatively important. To the long-standing discussions about photochemical oxidant formation, Phoenix has added questions about atmospheric perchlorate formation. Most recently, localized release and eventual decomposition of methane has been detected in the martian atmosphere [11]. Lacking any evidence of current volcanism on Mars, the source of such releases seem limited to sublimation of existing clathrates or biogenic sources. Confirming this observation and determining the genesis of the methane is clearly a high exploration priority.

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ACID ALTERATION OF BASALTIC SAND: FORMATION OF A MAJOR MARTIAN SURFACE TYPE.

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Introduction: The north polar sand sea of Mars is the type locality for the silica-rich TES Surface Type 2 (ST2) unit [1], but the nature of ST2 is not well constrained. Possible compositions for ST2 include high-Si volcanic glass, zeolites, and high-Si amorphous phases [1-4]. As no major volcanic edifices have been conclusively identified in the north polar region (NPR), it has been suggested that ST2 may form as a result of alteration of primary lithics. Indeed, recent studies have provided evidence for aqueous alteration of NPR deposits during the Amazonian [5-7]. Here we present new evidence from OMEGA near-IR spectra that ST2 contains iron-bearing glass and high-Si amorphous phases, likely formed via acidic aqueous alteration of typical martian olivine-rich basaltic sand.

Data: We have analyzed 0.37 to 2.5 μm OMEGA data north of 70°N from the first year of northern summer observations ($L_s=90-125^\circ$). The spectra were atmospherically corrected [7], stereographically projected into a north polar mosaic, and smoothed with a boxcar smoothing algorithm.

Results: Fig. 1 shows a representative OMEGA spectrum from the unit that we have classified as the most consistent with TES ST2. The spectrum has a wide and shallow absorption band centered near 1.1 μm , a broad reflectance maximum near 0.68 μm , and a concave continuum (steep and negative between 0.7 and 1.5 μm , but relatively flat beyond 1.5 μm).

A ~ 1.1 μm band with no band near 2 μm is consistent with iron bearing glass (e.g., lunar volcanic glasses in [8]). The presence of this band indicates no more than minor ($\sim 5\%$) pyroxene, which typically obscures the presence of glass. Spectra with this band are present throughout the NPR, but are concentrated within particular sources in the polar layered deposits and Siton Undae (SU), the extensive dune field south of Chasma Boreale. SU also has some of the strongest values of the TES 465 index [1], which detects ST2.

While negative (blue) slopes due to thin ferric coatings are common on Mars, the concave slope we have observed in the NPR is unique, and is an excellent match for the spectra of thin (~ 3 μm), Si-rich alteration coatings on Hawaiian basaltic glass [9] (Fig. 1).

Discussion: Relatively thick (10^2 's – 100 's of μm) Si-rich rinds are common on Earth, and are thought to form via alteration of Si-rich surface particles [10]. The similarity of the SU spectra to those of the thinnest coatings of [9] implies that these coatings are uniformly thin and likely to form from minor surface alteration of the grains. In Hawaii, this process occurs

due to contact with sulfuric acid (pH 3-4) rain. At these pH levels, Si, Al, and Ti are retained while lower valence cations are removed from the leached layer [9].

While these Si-coated, glassy deposits may be produced by alteration of glass-rich volcanic ash, leaching of typical martian olivine-rich basaltic sand may also explain the lack of other ferrous minerals that would otherwise obscure the glass absorption bands. In leaching experiments at low pH (<1) with olivine-rich basaltic sand, olivine is much more reactive than glass, and dissolves to leave amorphous-Si and sulfate coatings on intact glass sand grains [11].

Implications: If the Si-coated basaltic glass sand grains of SU are representative of the global ST2, then the acidic alteration that produced them may also be a widespread process. The association of strong ST2 signatures with high-latitude terrains [1] may indicate that the source of the water for alteration is related to the climatic shifts that occur during obliquity cycles. Additional evidence may be present at the Phoenix landing site. The translucent to opaque brown sand/silt particles observed by the Optical Microscope have been suggested to be altered volcanic glass, and rinds may have been observed on black, presumably ferrous sand particles [14].

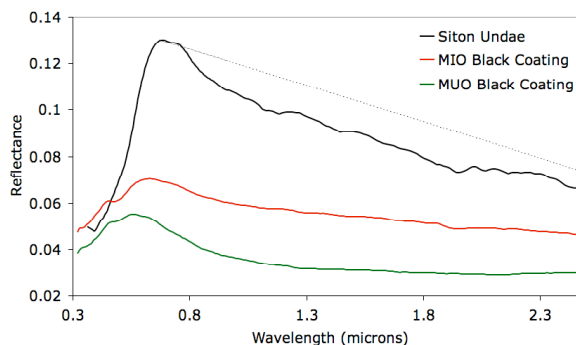


Figure 1: SU (72.1°N, 315.7°E) OMEGA spectrum compared with Si-rich coatings on Hawaiian basaltic glass [9]. Negative and concave cont. may represent a linear combination of ferric and Si-coatings.

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METHANOGEN GROWTH IN PERCHLORATE-SUPPLEMENTED MEDIA AND IMPLICATIONS FOR LIFE IN PHOENIX-TYPE SOILS

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Introduction: Perchlorate (ClO_4^-), a highly oxidizing compound, was identified on the martian surface by the Phoenix Lander at concentration levels up to 1.0% [1,2]. There is some debate as to whether an environment with perchlorate salts is too harsh for any organism to survive. Methanogens are able to survive in a numerous unwelcoming environments. Due to their ability to survive in extreme conditions, these anaerobic chemototrophs may have been the first autotroph to evolve on Earth, making them a good candidate for life on Mars [3]. In this project we studied the survivability and growth of methanogens in perchlorate solutions relevant to Mars [2].

Methods: Four methanogen species (*Methanothermobacter wolfeii*, *Methanosarcina barkeri*, *Methanobacterium formicicum*, and *Methanococcus maripaludis*) were used to test for possible methanogen growth in three perchlorate salt media (sodium, potassium and magnesium). The methanogen species were chosen due to their previous success of surviving in Mars-like conditions [3]. A specific medium was prepared for each species; CO_2 was added as an energy source and H_2 for an energy source. Perchlorate salt solution at different concentrations was added to the sterilized beakers. Tubes were inoculated with the appropriate organism and methane growth was measured by gas chromatography.

Results and Discussion: Although methane concentrations varied with species and salt tested, all four species of methanogens produced detectable amounts of methane at all concentrations of each tested salt (Fig. 1). In all cases, there was little to no difference in methane concentrations at 0 and 0.1% perchlorate. In most cases, 1.0% perchlorate resulted in, initially, lesser amounts of methane. There are at least two possible explanations for this. The higher perchlorate concentrations may be inhibiting methane production by the methanogens. A second explanation would be that methanogenesis is not being inhibited, but the methane being produced is being oxidized by the perchlorate, resulting in less methane being measured in the headspace of the culture tubes. In some cases methane concentrations in the higher-concentration perchlorate tubes eventually reach the level of the control, supporting the second explanation.

Implications for Mars: Although methane in the Martian CO_2 atmosphere is globally very dilute, about

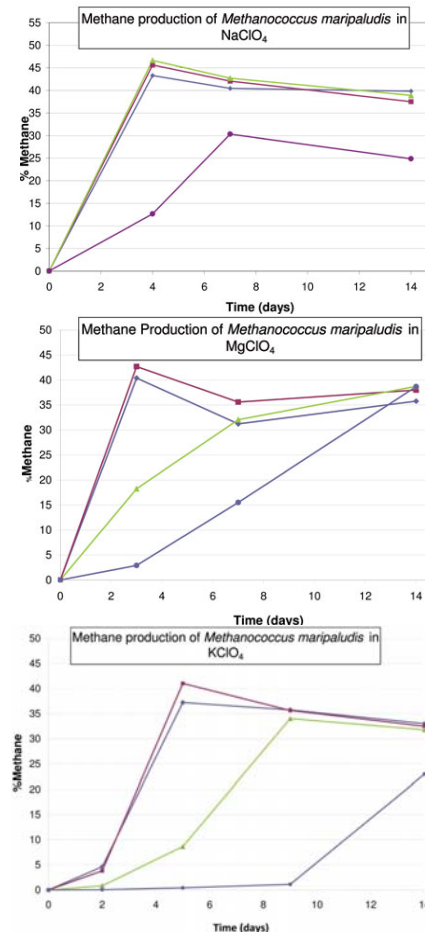


Figure 1. Methane concentrations in *Methanococcus maripaludis* cultures exposed to three perchlorate salts. Diamonds represent the control, squares the 0.1% perchlorate, triangles the 0.5% perchlorate and the circles 1.0% perchlorate.

10 ppb, there are localized areas where the concentrations are as high as 35 ppb [4] and must be constantly replenished due to photochemical losses [5]. These localized areas and concentrations cannot be explained by impacts or volcanism [5] and may be areas where methanogens are producing methane. Results here indicate that the perchlorates discovered by the Phoenix lander would not necessarily rule out the presence of these methanogens on Mars.

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WHAT WOULD MER SOIL DO IN THE PHOENIX WCL? J.A. Hurowitz¹, ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 joel.a.hurowitz@jpl.nasa.gov.

Introduction: The Phoenix Wet Chemistry Laboratory (WCL) has yielded fascinating new information on the nature of soluble minerals present in soils at the northern latitudes of Mars. Put simply, the WCL was designed to soak a soil sample in water and analyze the chemistry of the soil leachate using sensors and electrodes mounted in the walls of the WCL sample cell [1]. Perhaps one of the most interesting results of this experiment was the finding that the soil leachate has a mildly alkaline pH [2].

In contrast to Phoenix soil, it might be expected that immersing a Martian soil from an equatorial latitude landing site (Mars Exploration Rover (MER), Pathfinder, Viking 1), all of which have very similar chemical properties [e.g., 3], would result in a relatively acidic pH. This expectation is borne of the high sulfur abundances in equatorial soil and dust, which have been assumed to be the product of interactions between the Martian soil and sulfuric acid-rich solutions [e.g., 4]. The influence of acidic, S-rich fluids has been confirmed by MER Mössbauer results, which indicate the presence of a variety of ferric sulfate minerals, which are diagnostic of low-pH (pH < ca.4.0) formation conditions [e.g., 5], and have the ability to acidify dilute fluids when dissolved [e.g., 6].

In order to test the hypothesis that the immersion of soil from an equatorial latitude landing site in water would result in a low-pH solution, a series of reaction path simulations will be presented in which the minerals present in MER soils are subjected to Phoenix WCL experimental conditions. These simulations will be carried out using *The Geochemist's Workbench*. The results of these simulations will provide insight into the aqueous chemistry of liquids in contact with soils at Martian equatorial latitudes, and provide a basis for comparison of Phoenix WCL results to soil chemistry from other landing sites on Mars.

Predicting the Behavior of an MER Soil Sample: For the initial simulations, the mineral abundances of MER soils will be taken from the work of [7], with igneous mineral compositions taken from [8]. Because the results from [7] do not uniquely identify chloride minerals, 0.75 wt. % Cl (generally consistent with abundances from all landing sites) will be added as a variety of chloride salts, including $\text{Mg}(\text{ClO}_4)_2$.

In an initial simulation (**Fig. 1**) a fluid composition identical to the WCL leaching fluid was used (TS21 from Table 2 of [1]) to evaluate how a soil from MER would behave in the Phoenix WCL. A pH of 5.6, also consistent with [1], was set at the beginning of the simulation. Following determination of the equilibrium

speciation in the initial solution, 1 cm³ of “soil”, whose mineral abundances and compositions are derived from [7] and [8], was reacted with the solution.

In the simulation shown on **Fig. 1**, all of the sulfate in the soil was assumed to be present as the Fe^{3+} hydroxy-sulfate schwertmannite, and no minerals were allowed to precipitate. Redox disequilibrium was assumed between Fe^{2+} and Fe^{3+} , and NO_3^- and NH_3 , and the igneous mineral phases were allowed to react with the solution kinetically using known laboratory dissolution rates (thereby minimizing their impact on solution chemistry). The simulation was conducted at 25°C.

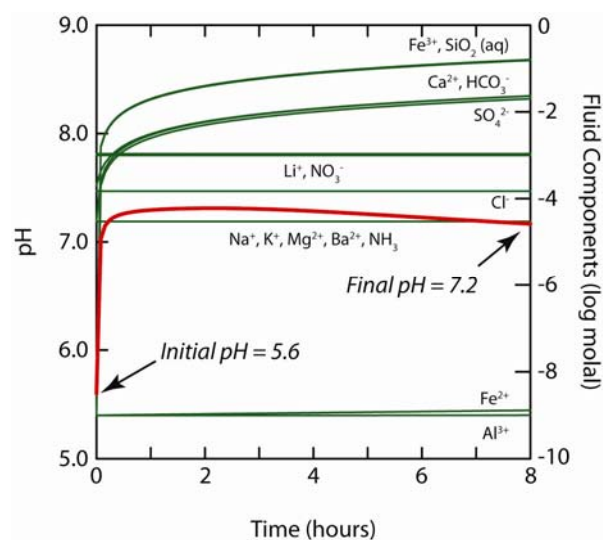


Figure 1: pH and fluid composition as a function of time following addition of soil to WCL leaching fluid.

The results of this simulation indicate that pH evolves from a value of 5.6 to 7.2 after 8 hours of MER soil - WCL solution interaction. Much work remains to be done to understand the implications of this interesting initial simulation, but this work provides a useful proof of concept for a new means of evaluating and comparing the aqueous chemistry of soluble soil minerals at different landing sites on Mars.

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AQUEOUS CHEMISTRY OF THE MARTIAN SOIL: RECENT RESULTS FROM THE PHOENIX MARS LANDER WET CHEMISTRY LABORATORY (WCL). S. P. Kounaves¹, M. H. Hecht², R. Anderson¹, K. Gospodinova¹, P. Hredzak¹, J. Kapit¹, J. Maisano¹, K. McElhoney¹, Q. Moore¹, G. O'Neil¹, J. Shusterman¹, S. Stroble¹, J. Wage¹, ¹Department of Chemistry, Tufts University, Medford, MA, 02155, ²Jet Propulsion Laboratory, Pasadena, CA, 91109. (samuel.kounaves@tufts.edu)

An important goal of the 2007 Mars Phoenix Lander [1, 2] was to analyze the chemistry of the soils, at the surface and at depth, to provide a better understand the history of the water, the biohabitability of the soil, the availability of chemical energy sources, and the general geochemistry of the site. To this end, the Phoenix included four wet chemistry laboratories as part of the MECA instrument package.

Each of the four identical WCLs (Figure 1) consisted of an upper assembly for adding soil, water, reagents, and stirring, and a lower beaker containing an array of sensors for determining the concentrations of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , H^+ (pH), SO_4^{2-} , NO_3^- , ClO_4^- , Cl^- , Br^- , and I^- . It also included electrodes for electrical conductivity, chronopotentiometric determination of Cl^- , Br^- , and I^- , and cyclic voltammetry[3].

The concentrations of the measured ionic species for one of the soil samples (Rosy Red) are shown in Table 1. The results were similar for all three soil samples analyzed, with soil-solution mixture dominated by ClO_4^- , Mg^{2+} , and Na^+ at mM levels, with sub-mM concentrations of Ca^{2+} , Cl^- , and K^+ .

Equilibrium modeling, using MINEQL, GWB, and FrezChem, has been used to predict and verify possible starting mixtures of minerals and salts. Even though multiple possibilities exist, a limited number have been selected as most plausible and used to formulate both simulant solutions and soil samples. The simulants have been analyzed using a WCL flight spare unit and results compared to those obtained on Mars. The models indicate a very complex system with the final species distribution sensitive to several variables, including ionic strength, pH, P_{CO_2} , $[\text{SO}_4^{2-}]$, and the minerals assumed to be in the sample. Results to date point to a solution most likely saturated in respect to both Ca^{2+} and Mg^{2+} , from calcite and magnesite. Models and laboratory experiments also confirm the likely presence of sulfate in solution and its potential titration by both intentional and unintentional addition of barium chloride.

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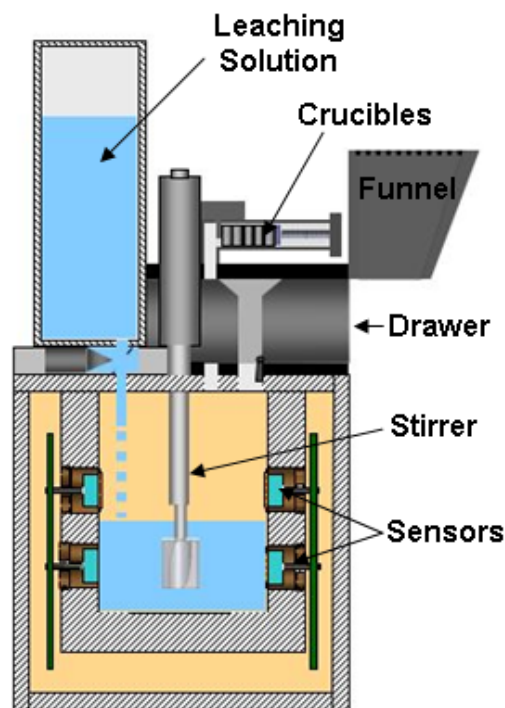


Figure 1. Diagrammatic cross-section representation of a single-use Wet Chemistry Laboratory (WCL)

Table 1 - Measured concentrations of ionic species in Rosy Red soil sample. Assumes delivery of a 1cm^3 sample with density of 1g/cm^3 .

Ionic Species	Concentration in Cell, mM	Est. %wt
Mg^{2+}	2.9 (± 1)	?
Ca^{2+}	0.6 (± 0.3)	3-5*
Na^+	1.4 (± 0.5)	0.10
K^+	0.4 (± 0.2)	0.03
ClO_4^-	2.6 (± 1)	0.75
Cl^-	0.6 (± 0.2)	0.04
pH	7.7 (± 0.3)	
* From TEGA Analysis [5]		

Geomorphology of High-Latitude, Ice-Rich Surfaces on Mars: Constraints on the Age, Thermal State, and Landscape Processes Active in Vicinity of Phoenix and the Martian Latitude-Dependent Mantle. J. S. Levy¹, J. W. Head¹, and D. R. Marchant², ¹Brown Univ. Dept. of Geological Sci., Providence, RI, 02912, ²Boston Univ. Dept. of Earth Sci., Boston, MA, 02215. joseph_levy@brown.edu

Mars is a natural laboratory for testing the physical and chemical processes that shape planetary surfaces under cold and arid climate conditions [1-3]. The Phoenix lander has discovered a wide range of chemical constituents [3-6] in samples of high latitude portions of the martian latitude-dependent mantle (LDM) [7, 8]. Critical questions remain as to whether the identified species formed in-situ or elsewhere, when the materials formed, and under what temperature and water-related climate conditions the unique Phoenix chemistry developed [3-6]? In particular, the origin and geological history of materials present at the Phoenix landing site provides insight into the origin and modification history of high latitude martian ice, yielding clues into the structure of martian latitude-dependent, ice-rich deposits, as well as into the thermal history of these young surfaces [7-10]: e.g., is the martian LDM composed of massive precipitated ice, or atmospherically cycled pore ice? Has (brine-mediated) melting played a major role in shaping the LDM, or are solid-vapor phase transitions dominant?

We present observations of the Phoenix landing site and vicinity from the Surface Stereo Imager and HiRISE [11-12] interpreted to indicate that the surface unit on which the Phoenix lander is present is geologically young (<100 ka) and has been domi-

nated by cold and dry geomorphic processes, rather than extensive wet or dry active layer cycling and/or churning (Fig. 1). No morphological evidence for geologically recent saturated soil conditions is observed at Phoenix landing site or across the martian northern plains. These observations suggest that chemical species requiring abundant water to form [3-6] were not produced recently in-situ at the Phoenix landing site, but rather have been mixed into the surface regolith from alternate (potentially impact-related) sources [13].

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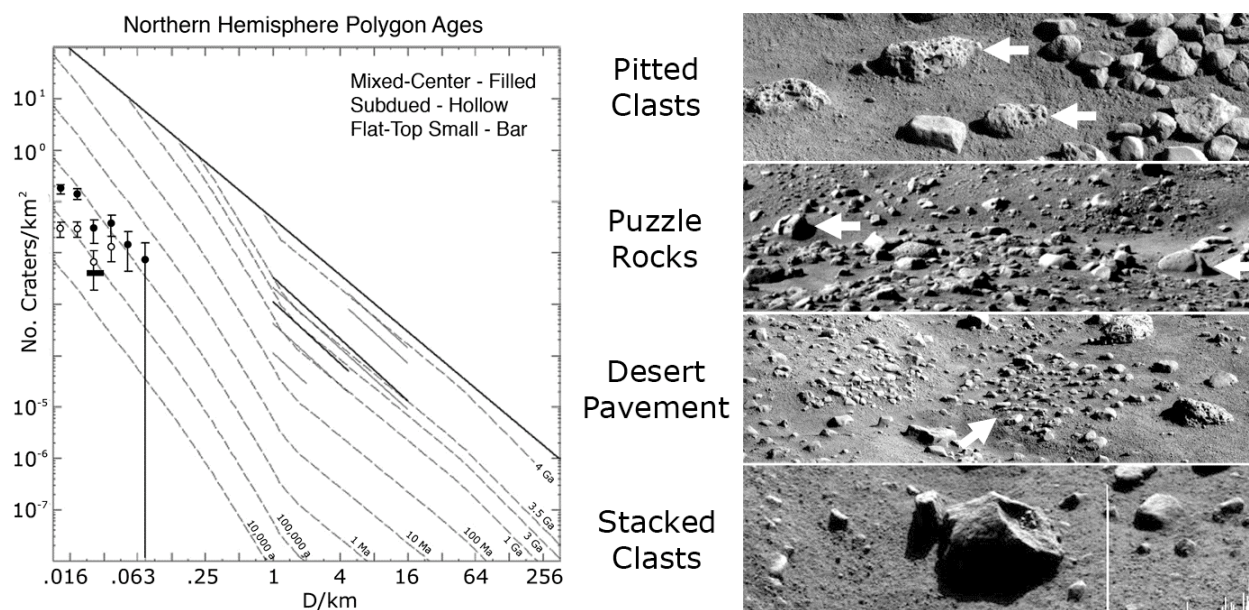


Figure 1. Left. Surface ages of polygonally patterned latitude-dependent mantle surfaces. Mixed-center polygons are typically found at ~45° latitude, subdued polygons at ~55° latitude, and flat-top small at ~65° latitude. High latitude icy surfaces on Mars are exceptionally young. Right. Landforms observed at the Phoenix landing site by the SSI interpreted to indicate a relatively stable, non-churning permafrost surface.

ELEMENTAL COMPOSITION AND HYDRATION OF MARTIAN REGOLITH BASED ON GAMMA AND NEUTRON SPECTROSCOPY DATA. M. L. Litvak, N. E. Demidov and I.G. Mitrofanov, Institute for Space Research, Moscow 117997, Profsojuznaya st. 84/32, Russia, mlitvak.iki@gmail.com

Introduction: Spectrometric measurement of regolith by Viking 1,2, Pathfinder, MER-A,B showed the presence of material with similar concentration of basic elements in all landing sites [1,2]. The homogeneous upper Martian soil is the result of primary basalts dominant occurrence and eolian mixing. From the other hand it is known (observed by different instruments during orbital measurements) that there are some locations with anomalous non volcanic rocks like phyllosilicates, chlorides or sulfates [3,4].

In our study we concentrated on the Mars Odyssey gamma ray (GRS instrument) and neutron spectroscopy (HEND instrument) data to distinguish both regions with basic elemental composition consistent with standard regolith model and regions with anomalous elemental composition. The last ones may show presence of different hydrated minerals.

Data and Method: We used GRS instrument Si, Fe, Al, Ca, Cl, S concentration maps [5] and H concentration map according to HEND instrument [6] to check if the concentration in each pixel of the global martian map is consistent with standard regolith model. This test was based on the assumption that standard regolith regions may be described by two-component model with concentration of Si, Fe, Al, Ca, Cl and S equal to mean concentration found by MER A,B and variable amount of water. Calculations based on Pearson criteria for different levels of confidence were performed to choose the best-fit elemental composition for each pixel.

Conclusions: Calculations showed that standard regolith occupy vast territory of old southern highlands [fig. 1]. It was also found that regions with anomalous concentrations of basic elements are located in northern lowlands with fewer smaller locations in highlands and in the Hellas area. The resulted map of hydration for standard regolith regions [fig. 2] represents the most developed map of water on Mars created both on the basis of hydrogen measurements and normalization on the concentrations of other basic regolith elements.

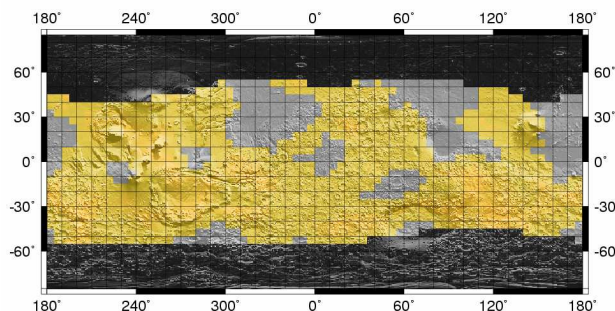


Fig. 1 Map showing location of regions formed with standard regolith (brown) and nonstandard regolith (grey)

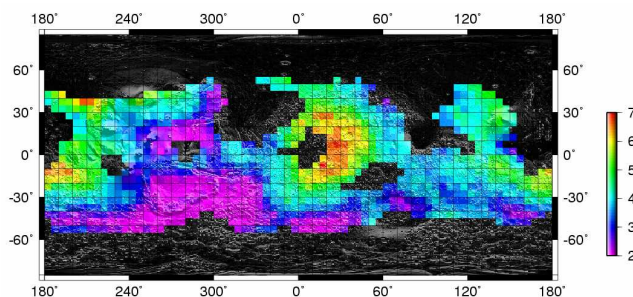


Fig. 2 Map of H₂O concentration in weight % for regions made by standard regolith.

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CLOSED SYSTEM CHEMISTRY INSIDE MASSIVE ICE DEPOSITS AT MERIDIANI PLANUM. P. B. Niles¹, J. Michalski², ¹Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058; ²Institut d'Astrophysique Spatiale, Université Paris Sud, Orsay, 91405, France. (paul.b.niles@nasa.gov)

Introduction: The discoveries made by the Opportunity rover at Meridiani Planum have provided a new view of the chemistry of the martian surface. These results have also spawned a number of different interpretations. These different interpretations of the chemistry of the Meridiani sulphate-bearing rocks can be categorized into two main groups. The first model suggests that the rocks are sedimentary and composed of a mixture of two components – a heavily weathered silicate component and an evaporite salt component [1]. The second model suggests the rocks are volcanoclastic and were weathered in place by sulphur rich gases [2].

We propose a third model [3] which suggests that individual grains or agglomerates of grains were weathered inside of a large dust/ice deposit, and were re-deposited into eolian sediments after the ice had been removed by sublimation. This hypothesis explains the available data better than the others for the following reasons: 1) The Meridiani sediments have basaltic cation compositions despite the fact that many of the cations are now associated with secondary weathering products such as sulfate [4]; 2) Only small variations in chemical composition are observed in the Meridiani sediments across the 16 km traverse of the Opportunity rover, and these changes are in MgSO₄ content alone, with little or no change in Fe, Ca, Na, or K [4]; 3) The cation composition of the Meridiani sediments shows a strong resemblance to the composition of the bright soils observed at the Pathfinder, Spirit, and Opportunity landing sites [4].

Model Description: This new model [3] for the provenance of the sediments at Meridiani Planum is based in principal on geochemical ideas pioneered by Burns [5], and sedimentological ideas proposed by Tanaka [6]. In our model, the sediments now located at Meridiani Planum were sourced from a nearby, massive dust/ice deposit that was located adjacent to Meridiani Planum. This massive dust/ice deposit formed through precipitation of ice around dust grains and aerosols during a period of high obliquity, and resembled the polar layer deposits that exist today in the martian north and south polar regions. Suspended dust in a Noachian atmosphere provided nucleation points for ice crystals to form which is an important driver for the precipitation of water ice in the present day polar caps [7] and would have been more prevalent on ancient Mars.

Exposure of the ice deposits to sunlight during the summer seasons allowed for radiant heating of dark grains within the water ice matrix. A similar effect has

been observed where radiant heating of soil grains, trapped in ice deposits in Antarctica, causes melting and migration resulting in the formation of aggregates [8]. The radiant heating led to the formation of thin water films sufficient to allow for reaction with the volcanic aerosols or sulphide minerals to create acidic solutions. The ice matrix provided a physical barrier enclosing each grain or aggregate of grains within a closed system environment at low temperatures with low water/rock ratios. The acidic solutions weathered silicate grains to form poorly crystalline aluminosilicates and sulphates [5]. The cold temperatures of the polar environment provided a mechanism for limiting water/rock ratios while simultaneously forming more concentrated solutions through freezing of excess solution.

A climactic shift (due to polar wander or obliquity changes) then led to conditions which favoured net sublimation of the massive ice deposit rather than deposition. The sublimation residue was made up of sand sized agglomerates of fine-grained, chemically weathered, and highly hydrated siliciclastic material mixed with sulfate salts. This material was reworked by eolian or impact activity. Burial of these highly hydrated phases caused the release of structural water that allowed limited diagenesis and blueberry formation to occur, but also prevented wholesale re-equilibration of the deposit and complete conversion of jarosite to hematite [9]. Small amounts of additional water may also have been supplied by brief ice melting events allowing for the possibility for surface runoff [1].

Implications: The weathering model proposed here could potentially explain the origin of many layered sulfate deposits on Mars, which share common characteristics: they are layered, occur in mounds and ridges, and lack an obvious provenance [10]. The sulfates are all exposed in spectrally detectable layered deposits that may have formed through eolian or impact reworking and transport of sublimation residue, or through episodic fluvial processes driven by limited melting of ice, or may reflect the original morphology of layered ice deposits.

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INFLUENCE OF GEOCHEMISTRY ON DETECTION OF BIO/ORGANIC SIGNATURES. C. D. Richardson¹, N. W. Hinman¹, J. M. Kotler¹, T. R. McJunkin², and J. R. Scott². ¹Department of Geosciences, University of Montana, Missoula, MT 59812 (nancy.hinmna@umontana.edu). ²Idaho National Laboratory, Idaho Falls, ID 83415 (jill.scott@inl.gov).

Introduction: Our primary interest is in determining how the geochemistry on Mars may affect the ability to detect signs of life via laser desorption/ionization mass spectrometry (LD-MS) techniques. The first LD-MS instrument that is scheduled to visit the martian surface is part of the Mars Organic Molecule Analyzer (MOMA), which is part of the ExoMars payload.

In conjunction with mineralogical data, the detection and identification of bio/organic signatures can assist in linking biochemical and geochemical processes. Geomatrix-assisted laser desorption/ionization (GALDI) in conjunction with laser desorption Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is a method of obtaining bio/organic signatures from a range of geological materials with little or no sample preparation [1]. A variety of laboratory and natural samples have been investigated to determine how well bio/organic signatures can be detected when associated with different minerals using GALDI-FTICR-MS [2]. Because the minerals essentially play the role of “matrix” to assist desorption and ionization of the bio/organic compounds, it is not surprising that some bio/organic-mineral combinations work better than others. Even for the minerals that work well, one of the key challenges is that the bio/organic constituents are not homogeneously distributed.

Approach: Laboratory or natural samples were analyzed with a 7T imaging laser desorption FTICR-MS, which has been described previously [3,4]. Each spectrum was acquired with a single laser shot using a wavelength of 355 nm with a 6 ns pulse for an irradiance of $\sim 10^8$ W/cm² for 10 μ m spot. In survey or mapping mode, the mass resolution was typically $\sim 10,000$ with a mass accuracy of 3 ppm.

Results & Discussion: Six general types of ionization reactions have been observed. (1) Organic compounds, such as polyaromatic hydrocarbons (PAHs), tend to self-ionize and not be dependent on the geomatrix present [5]. (2) Not unexpectedly, evaporitic minerals with alkali metals present tend to produce cation attached bio/organic signatures [1]. (3) While this is generally true of alkyl halides, if sulfate is the counterion, then larger inorganic cluster ions are formed (usually noticed in the negative mode) that can have gas-phase basicities that allow them to abstract a proton from a bio/organic molecule to produce a deprotonated bio/organic ion [6]. (4) The presence of sulfate can also lead to the production of complex cluster ion bio/organic signatures, similar to that observed with

glycine and jarosite [2]. (5) Fragmentation of bio/organic compounds has also been observed, predominantly with iron oxide minerals [1]. (6) It is also possible for the presence of certain bio/organic compounds (i.e., PAHs) to assist in the ionization of other bio/organic compounds [1].

Because a combination of these reactions may be possible in a natural sample, the bio/signature ultimately observed via GALDI-MS is dependent on the competitive nature of the possible ionization mechanisms. A key example of the competition between reaction mechanisms is the case of aromatic amino acids with the mineral thenardite (Na₂SO₄). Aromatic amino acids by themselves behave similar to PAHs and will self-ionize with UV laser desorption/ionization (Fig. 1A). When mixed with the mineral thenardite, the aromatic amino acid, tyrosine (Tyr, C₉H₁₁NO₃), is preferentially ionized by cation attachment (Fig. 1B).

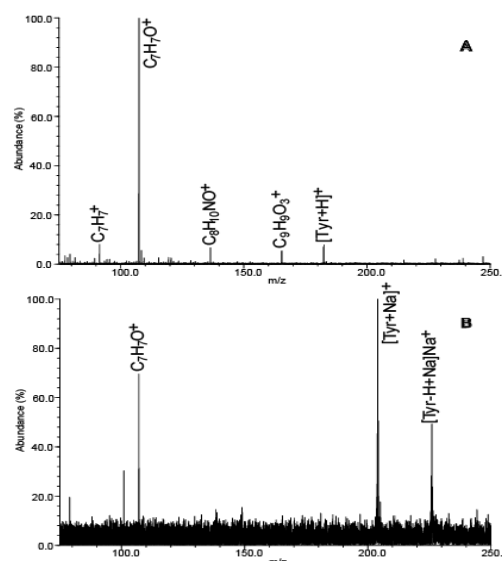


Figure 1. FTICR-MS spectra of (A) tyrosine alone and (B) tyrosine with thenardite [7].

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TIME DEPENDENT MODEL FOR WATER VAPOR DIFFUSION/ADSORPTION AND HEAT TRANSFER AT THE PHOENIX LANDING SITE. E. G. Rivera-Valentin¹ and V. F. Chevrier¹, ¹Arkansas Center for Space and Planetary Sciences (eriverav@uark.edu), University of Arkansas Fayetteville

Introduction: Phoenix has shown that there exists vapor pressure variations on a diurnal time scale, which are not predicted by the GCM [1]. Recorded vapor pressures by the TECP shows systematic variations by about 2 orders of magnitude (Fig. 1) [2]. Since the GCM model does not take into account atmospheric interactions with the regolith, we may infer that the shortcomings of this model in this polar region implies that such interactions are significant [2]. Possible processes that may account for such a coupling include adsorption onto regolith grains as well as hydration of perchlorate [2] or equilibrium with a liquid phase [3].

We investigate the effect of adsorption as a potential sink for water vapor [4,5]. We are creating an integrated numerical model that accounts for both heat and mass transfer of water vapor in the regolith, including the effect of adsorption [4]. Using this model, we can simulate the effect of adsorption on humidity and attempt to relate this to Phoenix observations.

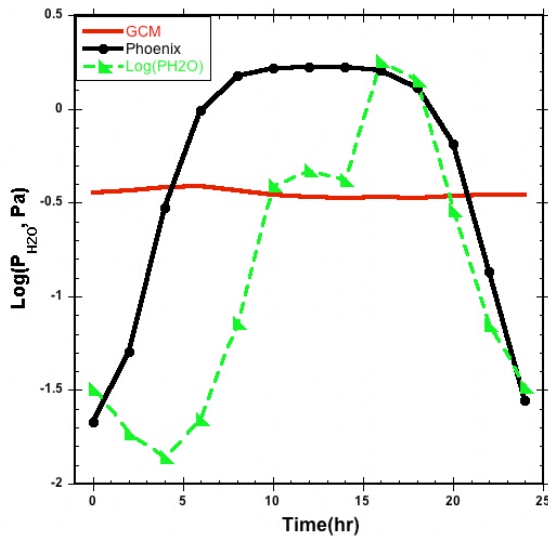


Fig. 1: Gaussian fit to water vapor pressure at the Phoenix landing site [2], compared to the results from the GCM model and our preliminary results.

Methods: To model heat transfer, water vapor diffusion, and adsorption in the regolith, we use COMSOL Multiphysics. We specifically focus on the kinetics of the various processes and their variations with temperature. Most other models focus on longer timescales where adsorption can be averaged [6]. This though is based on the cyclicity of the adsorption process and the assumption that the process occurs instantaneously. However, recent studies have shown that slow adsorp-

tion kinetics can strongly affect the diffusion of water vapor [4]. Thus, the study of water behavior on short timescales requires the inclusion of the adsorption kinetics and a detailed study of the transient effects.

Heat Flux Model: We primarily use the equation set proposed by multiple authors to model the heat flux incident on the Martian surface [7]. We take into account the diffusion of the direct solar beam, the indirect solar illumination due to scattering, and thermal emission of the atmosphere.

Mass Transfer Model: The differential equation [4] for the transport of water vapor allowing for simultaneous diffusion and adsorption in the Martian regolith is:

$$\frac{\partial p}{\partial t} \left[1 + \Psi \frac{\partial \theta}{\partial p} \right] = \frac{\partial D}{\partial z} \frac{\partial p}{\partial z} + D \frac{\partial^2 p}{\partial z^2} \quad (1)$$

where p is the partial pressure of water vapor, D is effective diffusion, z is a depth parameter, Ψ is a constant that corresponds to the thermodynamic part of the adsorption process and is defined as:

$$\Psi = \frac{RT_s \rho_{H_2O} \rho_{reg} A_s l}{M_{H_2O}} \quad (2)$$

where R is the ideal gas constant, T_s is the temperature of the surface, ρ_{H_2O} is the density of water, ρ_{reg} is the density of the regolith, A_s is the specific surface area of the regolith, l is the thickness of the adsorbed water monolayer, and M_{H_2O} is the molecular weight of water.

Results: At this moment, we have fully developed the heat flux model. We are in the process of integrating the heat flux and mass transfer models. Figure 1 shows our preliminary model results. The result shown is merely a simulation over 7 sols assuming warmest day conditions for every sol.

Conclusion: From Fig.1, we see that our model correlates well with evening humidity values, but does not with morning values. By simulating the mass transfer process at the Phoenix landing site, our model will help in understanding the observed vapor pressure variations. In addition, we will make a versatile model that will also include phase change and thus help determine if liquid water can form under present-day conditions.

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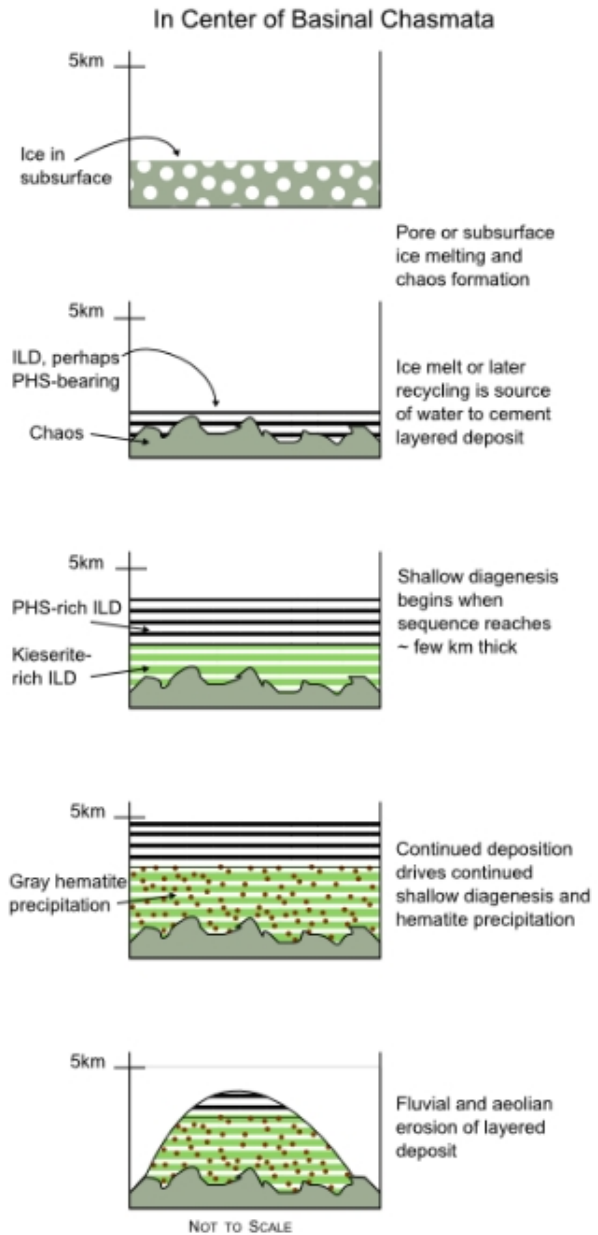
SULFATES IN VALLES MARINERIS AND IMPLICATIONS FOR MARS' AQUEOUS HISTORY. L.H. Roach¹, J.F. Mustard¹, S.L. Murchie², and J.L. Bishop³, ¹Brown University, Box 1846, Providence, RI 02912. Leah_Roach@brown.edu, ²Johns Hopkins/APL, Laurel, MD 20723, ³SETI Institute/NASA-ARC, Mountain View, CA 94043.

Introduction: Mapping the type and distribution of hydrated mineralogy is one way to track the aqueous history of Mars. Sulfates are a potentially good tracer of past climate because they form by aqueous processes, so their presence, volume, and process of formation can characterize how much water was available. The sulfates in Valles Marineris (monohydrated Mg or Fe sulfate and polyhydrated sulfates (PHS) of undetermined cation(s)) occur in regionally consistent stratigraphy with red hematite. Together, the alteration mineral assemblage may represent earlier shallow diagenetic alteration.

Datasets: Mapping of sulfate distribution was extrapolated from spectral interpretation of near infrared CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) data at targeted (~20 m) and mapping (~200 m) resolution [1]. HiRISE (High Resolution Imaging Science Experiment) [2] and CTX (Context Imager) [3] data were used to extend sulfate mapping beyond CRISM coverage. Red hematite and other iron phases were identified through spectral analysis of visible CRISM wavelengths (0.4-1.0 μm).

Spectral results: We identified kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), PHS of unknown cation(s), red hematite, and other, undetermined ferric phases in light toned layered deposits within many of the Valles Marineris basinal chasmata (Capri, Candor, Melas, Ophir, and Ganges) [4]. Gray hematite had previously been mapped in many of the same locations [5, 6].

Stratigraphic results: The stratigraphy of sulfates and iron oxides in the light toned layered deposits across the basinal chasmata had several key elements in common: (1) PHS on top of kieserite in a horizontal contact; (2) crystalline red hematite associated with kieserite bedrock but not with PHS; (3) other ferric oxides sometimes present at the base of the sulfate-bearing layered deposits. Fig 1 is a schematic for how the alteration materials could collect in layered deposits within basinal chasmata. One plausible formation process is that the kieserite and crystalline red and gray hematite could have formed by diagenesis of sulfate-bearing sediments as a consequence of burial and/or a higher heat flow early in the chasma's history. This diagenetic process would be active in the lower parts of any deposit > few km; upper units would remain unaltered. Shallow diagenesis of sulfate-rich sediments may be responsible for the sulfate and iron oxide stratigraphy expressed today throughout Valles Marineris.



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SUBSTRATE STEREO SELECTIVITY MAY BE USED TO DISTINGUISH BETWEEN CHEMICAL AND BIOLOGICAL REACTIVITY ON MARS. Henry J. Sun, Desert Research Institute, 755 E. Flamingo Road, Las Vegas, NV 89119. henry.sun@dri.edu

In the Viking labeled release experiment, organic compounds added to the Martian soil were rapidly degraded as if the soil contained live microorganisms [1]. But failure to detect native organic carbon raised the possibility of a chemical reactivity as caused by the presence of inorganic oxidants [2, 3]. The debate between pro-life and anti-life views is likely to intensify in light of the results of the Phoenix mission, which could be argued to support both possibilities. Future astrobiology studies of Mars need a simple method to distinguish between chemical and biological reactivity. One idea, as advocated by Dr. Gilert Leven and implemented by the Mars Oxidant experiment, is the use of pure enantiomers of chiral compounds [4]. The idea assumes that biological activity is inherently stereo specific, whereas abiotic redox processes are stereo indiscriminate. In this presentation I present experimental data indicating that this assumption is valid, but not across the board for all chiral substrates. In the case of glucose, the assumption appears to be correct. More than two dozens of species of microorganisms, including bacteria, eukaryotic yeasts and fungi, and archaea, have been studied so far. They all consumed D-glucose. None used L-glucose [5]. Microbial communities in four different soils, too, consumed glucose in a stereo specific manner. In the case of lactate and amino acids, two substrates that were used by the Viking labeled release experiment, the result was mixed. Some organisms utilized only D-lactate and only L-amino acids as has been assumed. Other organisms were stereo indiscriminate and used L-lactate and D-amino acids as well as D-lactate and L-amino acids. For some amino acids a third scenario exists, where both enantiomers were biologically active, but the L form was more

so than the D form. The addition of these enantiomers to soils was followed by a lag phase whose duration is enantiomerically dependent. The lag phase was consistently shorter for the natural enantiomer, L for amino acids and D for lactate, than for the rare enantiomers. Once they entered their respective log phase, the two enantiomers were consumed at approximately equal rates. In conclusion, stereo specificity or selectivity could be used to differentiate between chemical and biological reactivity, but such experiments would require a careful selection of substrates and need to take into account reaction kinetics.

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SUMMARY OF RESULTS FROM THE MARS PHOENIX LANDER'S THERMAL EVOLVED GAS

ANALYZER. B. Sutter¹, D.W. Ming², W. V. Boynton³, P. B. Niles², J. Hoffman⁴, H. V. Lauer⁵, and D. C. Golden⁶
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Introduction: The Mars Phoenix Scout Mission with its diverse instrument suite successfully examined several soils on the Northern plains of Mars. The Thermal and Evolved Gas Analyzer (TEGA) was employed to detect evolved volatiles and organic and inorganic materials by coupling a differential scanning calorimeter (DSC) with a magnetic-sector mass spectrometer (MS) that can detect masses in the 2 to 140 dalton range [1]. Five Martian soils were individually heated to 1000°C in the DSC ovens where evolved gases from mineral decomposition products were examined with the MS. TEGA's DSC has the capability to detect endothermic and exothermic reactions during heating that are characteristic of minerals present in the Martian soil.

The EGA detected water in the Phoenix soil. There was a low temperature water release beginning at 295°C that gradually rose to 735°C which was followed by a higher temperature water release [2] (Fig. 1). The initial water release could be attributed decomposition of hydrous carbonate or sulfate phases (e.g., hydrous magnesite, jarosite) or dehydroxylation of Fe-oxyhydroxides or phyllosilicates. The higher temperature water release could be attributed to dehydroxylation of phyllosilicates or serpentine or other rock forming minerals [2].

The higher temperature data indicated the presence an endothermic peak with an onset temperature at 730°C with corresponding CO₂ release. The most logical candidate material that exhibits these properties at this high temperature is calcite (CaCO₃ → CaO + CO₂) [3]. TEGA enthalpy determinations suggest that calcite, may occur in the Martian soil in concentrations of ~3 to 5 wt.% [3]

One of the main goals of the TEGA instrument was to detect the presence of organics in the Martian soil. Unfortunately no organic fragments were detected by TEGA's mass spectrometer. The Wet Chemistry Laboratory (WCL) did detect perchlorate in the soil [4]. TEGA's MS detected a mass 32 peak between 325 and 625°C in the soil Baby Bear which was presumed to be oxygen (O₂) derived from perchlorate decomposition [4]. Organics if present would decompose at these same temperatures and would unfortunately be oxidized to CO₂ by the O₂ [5] The Phoenix soil exhibited a low temperature (200 to 600) CO₂ release which could be attributed to oxidized organic material, decom-

position of Fe- or Mg-carbonates, and/or desorption of adsorbed CO₂ [3].

The Phoenix Lander TEGA instrument detected water at temperatures that may indicate the presence of phyllosilicates, Fe-oxyhydroxides, and possibly hydrous carbonates, and/or hydrous sulfates. TEGA along with WCL detected calcite with a high degree of confidence. O₂ release from perchlorate decomposition may be why organics were not detected by the Viking GC/MS [5]. The release of O₂ from perchlorate decomposition will have implications on how future missions will conduct the search for organics on Mars. If perchlorates are ubiquitous on Mars and if organic detection techniques require heating then leaching of the soil will be required to remove soluble perchlorate. Solution techniques (e.g., super critical water extraction) [6] that extract organics without heating may provide an alternative way to obtain organics for analysis without organic destruction.

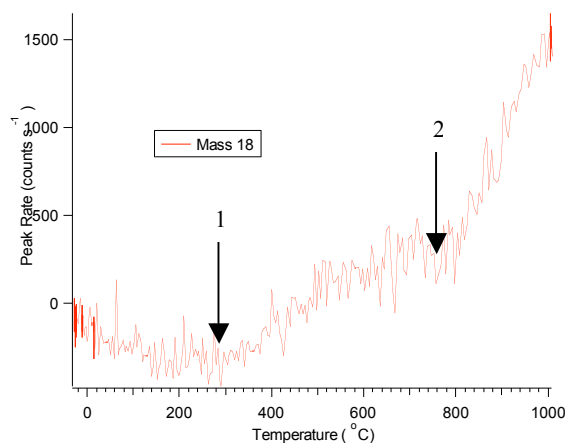


Fig. 1. Water release from the Phoenix surface soil, Baby Bear. Initial release occurred at 295°C (arrow 1) followed by significant water release at 735°C (arrow 2).

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Understanding the Evolution of Martian Carbonates from a Combined Modelling and Synthesis Study

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Introduction – There were several discoveries in 2008 regarding carbonates on Mars that are important in understanding the evolution of these salts. These include the identified CaCO_3 by Phoenix's TEGA and MECA instruments [1,2]. The Phoenix lander has also discovered the surrounding soils were pH alkaline (8.3 ± 0.5) [2] and enriched with subliming water ice, both conditions favourable to carbonate formation. Furthermore carbonates (in the form of MgCO_3) were detected by reflectance spectra from the orbital IR and VNIR spectrometer CRISM [3]. Despite these discoveries, without material being brought back directly from Mars by a sample return mission, martian meteorites provide the best source for analysis of the fine-scale mineralogy of the martian surface.

ALH84001 – The origins of ALH84001 carbonates are of great importance for understanding the ancient martian environment. Thought to have formed ~ 3.9 Ga [4], they are assumed to have precipitated from fluids with neutral to alkaline pH in contact with CO_2 . Approximately 0.6 Ga separates primary crystallization of ALH84001 from formation of secondary mineral assemblages. The period in which the carbonates formed has been called the Phyllosian era, owing to the outcrops of phyllosilicates discovered by the OMEGA and CRISM spectrometers [5, 6]. Their ancient age, abundance and mineralogical variations make ALH84001 carbonates ideal candidates to provide insights into early martian environmental conditions.

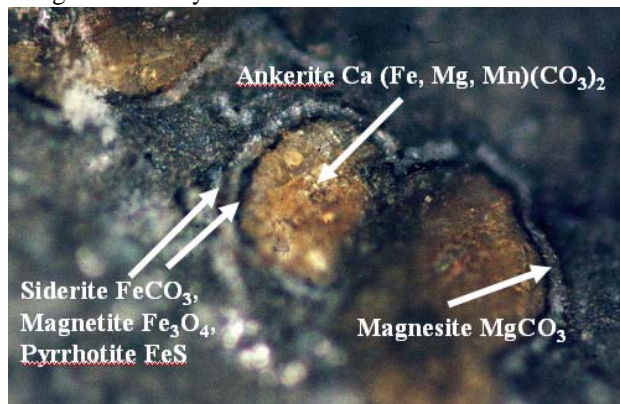


Figure 1 – Microscope image of rosettes within ALH8001, split 126.

We are investigating the formation conditions of carbonates in ALH84001 through two avenues:

(1) Modelling: We are attempting to constrain the carbonate precipitation environment by modelling how changes in fluid and atmospheric composition, oxygen

fugacity, temperature, etc change the final precipitation products. We are using the Geochemist Workbench™ (GWB) program to assist with modelling the Mg-Fe-Ca system. A variety of initial concentrations will be combined with CO_2 fugacities and temperatures to assess the effect of each variable on the system. It should be possible to model the evolution of the carbonate assemblage as water evaporates, at set P/T conditions (or with 'sliding' variables) with some constraints on either Eh/ O_2 fugacity and partial pressure/fugacity of CO_2 .

(2) Synthesis: In order to determine the boundary conditions for precipitation, without straying into kinetically, or thermodynamically, unviable environments, we are also producing synthetic carbonates from fluids of known composition at known temperatures, following on from the precipitation experiments by Golden et al. [7, 8]. The resulting samples will then be characterized by XRD and SEM for compositional analysis, imaging and mapping. We will compare the synthesized carbonates with carbonate rosettes from ALH84001 to ensure that our derived environments are realistic for the martian surface. Solution compositions from our synthetic carbonate production experiments, as well as simulated or approximated compositions taken from literature [7, 9] will define the initial starting conditions for the modelling.

Future work – Once characterization of ALH84001 has been completed we will use GWB and our synthesis chambers to investigate the carbonate formations discovered by Phoenix. The ionic values obtained from MECA combined with surrounding mineral characterisation from CRISM will be used to produce candidate aqueous solutions.

Implications – The results from modelling and carbonate synthesis will help reveal the conditions of the period on Mars that is of greatest interest for future missions when the planet may have had a 'warm and wet' environment. The results from planned future work will provide insights into more recent cold and dry environment and how aqueous solutions have evolved over the history of Mars.

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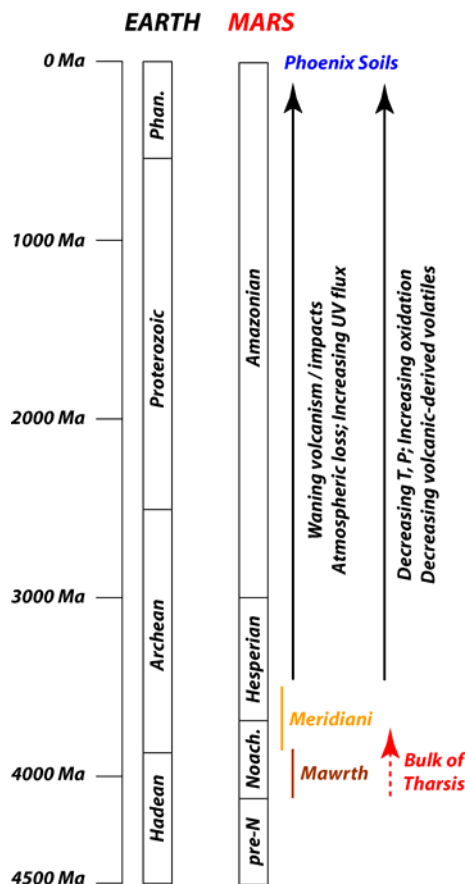
THE CHEMISTRY OF MARTIAN WATER AFTER ~3GYR OF PLANETARY EVOLUTION. N. J. Tosca,
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Introduction: Our present knowledge of water on Mars is biased toward the ancient sulfate- and phyllosilicate-bearing sedimentary record – the product of liquid water’s larger role in concert with vigorous sedimentary processes [1]. But the unfamiliar chemistry and mineralogy uncovered by the Phoenix Lander reflect physical and chemical processes of a different climate – one that has resulted from billions of years of planetary evolution. When comparing orbital and *in-situ* evidence for liquid water on ancient Mars to the geologically recent Phoenix landing site, it seems important to ask: *What changed over time? And how did large scale planetary evolution change water’s chemistry as well as its role in shaping surface mineralogy?*

Water on ancient Mars: The weight of available evidence for liquid water on Mars rests largely in Noachian and Hesperian aged materials [1-3]. Ancient outcrops containing weathering products & chemical precipitates show that water was at times abundant on early Mars. At the same time, geomorphologic and mineralogical constraints suggest that even on ancient Mars the presence of liquid water may have been episodic and of limited persistence on a global scale [4].

Major influences on aqueous chemistry through time: Impacts and volcanism were the hallmarks of late-Noachian/early-Hesperian climates [5]. What the early/mid-Noachian phyllosilicate-bearing materials reflect of the ancient atmosphere is still not clear. However, late Noachian valley networks and the increasing role of volcanism do argue for at least a transient atmosphere and a geochemistry influenced by volcanic-derived volatiles (e.g., SO_4) [6].

In contrast, Amazonian climates saw waning volcanism and impacts, in addition to large-scale atmospheric loss [5]. Where and when H_2O was present during this time, it was largely in the form of ice and snow-pack, with glaciation driven largely by orbital parameters [7]. During these episodes there may have been regional melting, but meltwater chemistry would have been influenced by a thin atmosphere depleted in most volatile constituents except for CO_2 . Redox conditions were undoubtedly more aggressive in post-Noachian climates owing to increased UV flux and Fe photolysis [8], as well as other photochemical products that may have been more efficiently cycled into the youngest regolith. Despite the cyclic nature of recent Amazonian climates, episodes of liquid water may have been individually short-lived; geologically young



weathering products are scarce and, where they are present, are diagenetically immature [4].

In comparison to our increasing knowledge of ancient martian environments, the Phoenix results are exotic and unfamiliar. At the same time, the increased importance of atmospherically-driven chemical cycles, evolving redox conditions, waning volcanism and seasonally driven processes in the late Amazonian are all likely to have played a role in forming and modifying Phoenix soils. The importance of such processes appears to be consistent with our knowledge of large-scale planetary change and expected influences on aqueous chemistry.

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Notes
